

ICOM COMMITTEE FOR CONSERVATION

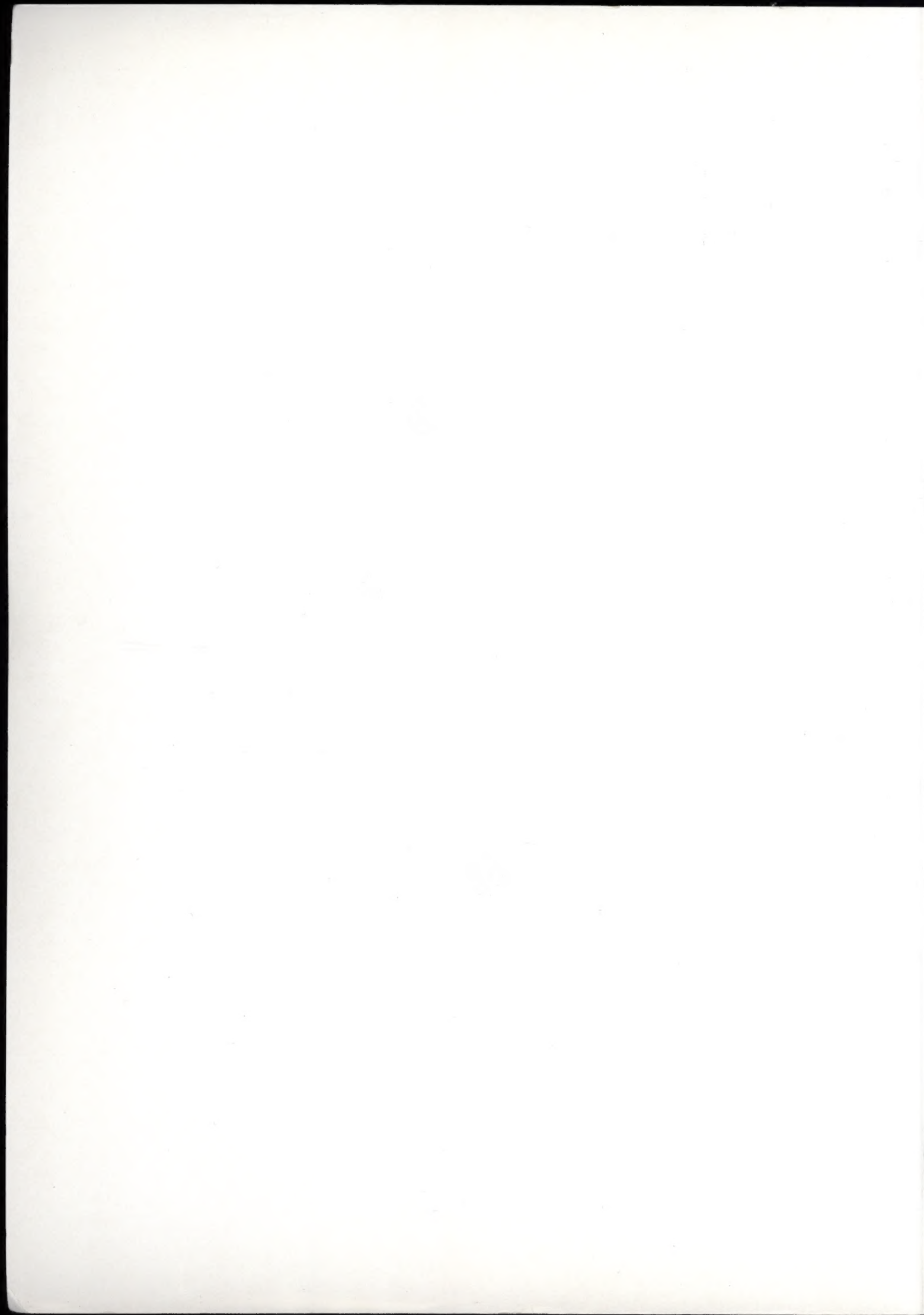
8th Triennial Meeting  
Sydney, Australia  
6–11 September, 1987

Preprints Volume I



COMITÉ DE L'ICOM POUR LA CONSERVATION











#### A NOTE ON THE COVER

The bark painting, ochre on stringybark, is by Bargudubu of the Gunwinggu tribe, Western Arnhemland. Borlung is one of the names given to the mythical rainbow snake who is the most revered totemic ancestor of Western Arnhemland Aborigines. She is believed to be the mother creator controlling human fertility, seasonal change, and the regeneration of nature. Borlung's spirit lives in water holes on Earth, often appearing as a rainbow arched across the sky or as rainbow hues in drops of water. Thunder is her voice raised in anger; lightning is her forked tongue flickering across the sky.

Photography by Jennifer Steele. Reproduced by permission of the Aboriginal Artists Agency, Sydney.

The hornbill wood carving (back cover) was made by the Abelam people of Papua New Guinea. The hornbill is an important totemic figure in the Abelam ceremonies and is normally attached to the figure in the Abelam ceremonies and is normally attached to the façade of men's spirit houses used for secret initiation rituals.

Photography by the Australian Museum. Reproduced by permission of the Australian Museum.

#### NOTE EXPLICATIVE SUR L'ILLUSTRATION EN COUVERTURE

Le tableau peint sur écorce d'eucalyptus, ocre sur écorce filandreuse, est l'oeuvre de Bargudubu de la tribu Gunwinggu, Terre d'Arnhem de l'ouest. Borlung est l'un des noms donnés au serpent arc-en-ciel mythique, l'ancêtre mythique le plus révééré chez les Aborigènes dans l'ouest de la Terre d'Arnhem. Il passe pour être la mère créatrice, qui commande à la fécondité des humains, au changement des saisons, et à la régénération de la nature. L'esprit de Borlung habite les trous d'eau sur la Terre et se manifeste souvent sous forme d'arc-en-ciel enjambant le firmament, ou sous forme de gouttes d'eau aux couleurs de l'arc-en-ciel. Le tonnerre est sa voix élevée en courroux; les éclairs sont sa langue fourchue oscillant dans le ciel.

Photographie: Jennifer Steele. Reproduction faite avec l'autorisation de l'Aboriginal Artists Agency de Sydney.

La sculpture sur bois du calao (en dos de couverture) a été exécutée par le peuple Abelam de Papouasie Nouvelle-Guinée. Le calao se veut une représentation totémique importante dans les célébrations rituelles des Abelams. Elle est généralement fixée à la façade des maisons des esprits, réservées aux rites secrets d'initiation chez les hommes.

Photographie: The Australian Museum. Reproduction faite avec l'autorisation de l'Australian Museum.



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#### EDITOR

Kirsten Grimstad

#### ASSISTANT EDITOR

JoAnn Hill

#### DESIGN

Sheila Levrant de Bretteville

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Leslie Stone

Debbie Swanson

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## Preface/Préface

The *Preprints* of the ICOM Committee for Conservation contain working papers of ongoing research or treatments that have been carried out during the period between the Committee's triennial meetings. They are intended as a basis for discussion among Working Group members and do not necessarily represent completed or refereed work in their areas.

In order to include the most up-to-date information possible, the *Preprints* are printed directly from camera-ready copy submitted by the authors.

Participants in the meetings of the ICOM Committee for Conservation are invited not as representatives of their country or institution but as specialists in their field.

This book is published by the Getty Conservation Institute, one of seven operating entities of the J. Paul Getty Trust. Other programs of the Trust are the J. Paul Getty Museum, the Getty Center for the History of Art and the Humanities, the Getty Art History Information Program, the Getty Center for Education in the Arts, the Museum Management Institute, and the Program for Art on Film, a joint venture with The Metropolitan Museum of Art in New York.

Les *Prétirages* du Comité de l'ICOM pour la Conservation contiennent des documents de travail relatifs aux recherches et aux traitements constamment poursuivis, qui ont été accomplis pendant la période intermédiaire entre les réunions triennales du Comité. Ces documents sont destinés à servir de base aux discussions menées entre les membres des groupes de travail et ne font pas forcément l'objet de travaux achevés ou arbitrés dans leur sphère de travail.

Les *Prétirages* sont imprimés directement à partir des textes prêts pour la photogravure, qu'ont soumis les auteurs, de manière à incorporer les renseignements les plus récents possibles.

Les participants aux réunions du Comité de l'ICOM pour la Conservation sont invités non en tant que représentants de leur pays ou de leur institution, mais en tant que spécialistes dans leur domaine.

Ce livre a été publié par l'Institut Getty de Conservation, un des sept programmes de la Fondation J. Paul Getty. Les autres programmes de la Fondation sont: le Musée J. Paul Getty, le Centre Getty pour l'Histoire de l'Art et des Lettres, le Programme Getty d'Information sur l'Histoire de l'Art, le Centre Getty pour l'Enseignement des Arts, l'Institut pour la Gestion des Musées, et le Programme pour l'Art par le Film, ce dernier mené en collaboration avec le Musée Metropolitain de New York.





# Working Group 1

Scientific Examination of Works of Art

Investigation scientifique des oeuvres d'art





COORDINATION DU GROUPE DE TRAVAIL "INVESTIGATION SCIENTIFIQUE DES  
OEUVRES D'ART"  
BILAN ET PERSPECTIVES

Christian LAHANIER  
Laboratoire de Recherche des Musées de France  
Palais du Louvre  
34 Quai du Louvre  
75041 PARIS Cedex 01

Le groupe "Investigation Scientifique des oeuvres d'art", dont les actions thématiques couvrent l'ensemble des collections, s'efforce d'appliquer les sciences exactes à la Conservation afin de répondre à sa double vocation matérielle et intellectuelle : transmettre et mieux connaître les témoins culturels qui font la richesse des musées.

Physiciens et historiens d'art, restaurateurs et ingénieurs s'associent à la poursuite de nouvelles études et s'attachent à mettre en commun les moyens nécessaires à la réalisation d'une conservation préventive et de restaurations fiables.

De nouvelles méthodes analytiques non destructives doivent être développées avec le concours d'Instituts de Recherche spécialisés. Les techniques scientifiques dans leurs développements les plus avancés peuvent et doivent être mises au service de la conservation. Nous verrons dans les communications suivantes la diversité des approches et des moyens mis en oeuvre. Une tendance commune se dégage par la fréquence croissante d'utilisation d'équipements lourds (scanner (1), tomographe, microsonde électronique à transmission, microsonde à effet Raman (2), spectrométrie à résonance magnétique nucléaire, accélérateur de particules (3 et 4), spectrométrie de masse, spectrométrie de résonance paramagnétique électronique, méthodes nucléaires (5)) afin d'apporter des solutions techniques aux problèmes exprimés de plus en plus finement sur le plan scientifique. Ces méthodes d'examen, d'analyse et de datation permettent d'opérer en surface ou à l'intérieur de la matière, de constater un état ou suivre la cinétique d'un traitement. L'analyse de la composition globale, même non destructive, est parfois abandonnée pour la mesure de l'hétérogénéité de composition des matériaux révélatrice de la technique de fabrication, du vieillissement, du milieu d'altération et de la fiabilité d'un traitement.

L'image et son exploitation par ordinateur sont à même de modifier considérablement les modes d'interprétation des documents scientifiques. La production croissante d'images digitales au moyen de caméras sensibles aux rayonnements visible, infrarouge (6 et 7) et ultra-violet ainsi qu'aux rayons X (8) nécessite de développer simultanément de nouveaux moyens de stockage. Le couplage de caméras à un ordinateur permettra de quantifier les paramètres d'une image (par exemple, graphisme d'un peintre : formes et tracé du dessin sous jacent, espacement et largeur des touches, orientation de l'éclairage) ou d'en améliorer la qualité en temps réel (suppression du réseau de craquelures, ou de la trame du support (bois, toile) de celle de la couche picturale, assemblage automatique des documents photographiques (réflectogrammes ou radiographies). La gestion automatique des bases images est non seulement utile mais indispensable à la conservation des documents et à la recherche. Si l'image conservée sur vidéodisque peut parfois suffire, la recherche en histoire de l'art et en particulier le traitement de l'image nécessitent une définition que permet seul actuellement le disque optique numérique.

Dans le cadre du groupe de travail "Investigation scientifique des oeuvres d'art", deux réunions ont marquées la période triennale 1984-87.

"L'investigation scientifique des peintures de Raphaël", animée par Madame Antonietta GALLONE GALASSI, a été organisée par le Politecnico de Milan et la superintendance pour les biens artistiques et historiques de la Lombardie occidentale (9). Ce symposium constitué de séances de communications et de tables rondes a permis de réunir des experts européens et américains et de produire des actes en cours d'édition.

La seconde réunion, dirigée par Mme Catheline Perier-d'Ieteren, a eu lieu dans le cadre de l'Université libre de Bruxelles. Le thème "Wateau : technique picturale et problème de restauration" était illustré par une exposition. Les actes sont édités sous forme d'un catalogue (10) par le ministère de la communauté française de Belgique. Le succès de ces réunions thématiques à caractère scientifique et historique montre à quel point le groupe de travail doit persévérer dans cette voie.

Les 24 communications de nos membres actifs seront présentées selon cinq catégories :

- 1) technique picturale et typologie d'altération.
- 2) chronologie des pigments et datation du support en bois
- 3) caractérisation des pigments organiques
- 4) nouvelles applications ou développement de techniques d'examen
- 5) nouvelles applications ou développement de techniques d'analyse

Malgré les efforts déployés par Madame Catheline Perier-d'Ieteren, coordinateur adjoint, à introduire de nouvelles activités au programme concernant l'histoire de la technique picturale des artistes, les historiens d'art montrent un intérêt modéré à s'intégrer à nos réunions triennales non thématiques.

#### 1) Technique picturale et typologie d'altération

Diane Wolfthal (USA : New York, Columbia University)

L'étude de 55 tableaux hollandais peints entre 1400 et 1530 sur toile parfois apprêtée fait apparaître sur six peintures, l'usage de la détrempe. La présence d'huile sur une crucifixion exécutée en 1434 est certainement le plus ancien exemple connu jusqu'ici.

Ingrid C Alexander (Belgique : Bruxelles)

Antonietta Gallone Galassi (Italie : Milan, Politecnico)

Lors de la restauration de la "Conversation sacrée", dernier quart du 15ème siècle, de Piero della Francesca, l'étude scientifique a révélé la stratigraphie suivante - peuplier couvert d'une toile rouge - gesso - couche de colle animale avec parfois une fine couche de blanc de plomb intermédiaire puis la couche picturale. Liant à l'oeuf (tempéra) en général mais aussi présence limitée d'huile et de résine prouvant l'influence de l'école hollandaise.

Segolène Bergeon (France : Versailles, Service de Restauration des peintures des Musées Nationaux)

Catheline Perier d'Ieteren (Belgique : Bruxelles, Université Libre)

Les altérations de surface d'un tableau dues à la technique picturale, aux restaurations et/ou au nettoyage, en modifient l'aspect. Elles en faussent sa lecture et l'appréciation stylistique. Une typologie des altérations de surface de la couche picturale établie par les auteurs pourrait servir de point de départ à l'élaboration d'une documentation photographique de référence des états de surface.

#### 2) Chronologie des pigments et datation du support en bois

Peter Klein (RDA : Hamburg, University)

L'identification d'un second réseau de croissance dendrochronologique différent de celui des chênes du sud de l'Allemagne pour des peintures sur chêne de Rembrandt, Rubens et autres peintres du 14ème siècle à 1650 a conduit à en découvrir l'origine. 30 peintures et 200 échantillons de monuments analysés à Gdansk s'identifient à ce type, prouvant son origine polonaise, expliquant la date limite d'utilisation 1650 et précisant l'échelle chronologique.

J R Lancelot, A Allegret, B Nens, Ch Lahanier, J Rens  
J P Rioux, (France : CNRS, CEA, LRMF)

L'analyse par spectrométrie de masse d'échantillons de blancs de plomb a permis de confirmer la constance des rapports isotopiques  $^{204}\text{Pb}/^{207}\text{Pb}$  du plomb européen avant 1800. A partir du 19ème siècle l'importation de plomb exotique américain modifie progressivement le rapport isotopique. La chronologie devrait être affinée par l'analyse des teneurs en éléments traces en opérant directement sur les coupes de peinture par microsonde nucléaire.



C Coupry, J le Marec, J Corset, M C Papillon, R Lefèvre, A. Duval, Ch Lahanier, J P Rioux (France : CNRS, Université de Creteil, LRMF)

L'analyse par microsonde à effet Raman d'échantillons de blanc de titane a permis de caractériser deux formes cristallines, anatase et rutile, et de les doser semi-quantitativement. L'utilisation conjuguée du microscope électronique à réflexion et à transmission confirme ces résultats et permet de déceler les éléments caractéristiques du rutile traité. La date de début de fabrication de ces pigments, conjuguée à celle de leur utilisation en peinture de chevalet, permettra d'authentifier des oeuvres du 20ème siècle.

### 3) Caractérisation de pigments organiques

John Winter (USA : Washington Freer Gallery of Art)

Nombre de pigments organiques jaune (camboge), rouge (anthraquinone), brun et violet rencontrés dans les peintures de l'Asie de l'est sont encore non identifiés. Le choix de la chromatographie en phase liquide pour l'analyse du gamboge répond à la double nécessité d'opérer sur des micro-prélèvements et de pouvoir le distinguer d'autres colorants. Les essais se sont révélés positifs dans des conditions expérimentales définies.

M de Keijzer (Pays Bas : Amsterdam, Central Research Laboratory for Objects of Art and Science)

L'application successive d'acide sulfurique concentré d'acide nitrique concentré et d'hydroxyde de potassium en solution alcoolique sur une coupe de peinture permet au moyen de réactions colorées de caractériser 5 pigments organiques modernes : le bleu et le vert de phtalocyanine, la transquinacridone liniaire, la dioxazine carbazole et le jaune Hansa. La méthode est simple, peu onéreuse, mais destructrice de la surface de l'échantillon.

Gerhard Talsky (RDA : Munich, Université)

Depuis 1856, 400 pigments organiques ont été fabriqués. Sur 250 pigments commercialisés depuis 50 ans, 60 ont été identifiés dans des peintures modernes. L'analyse est effectuée au spectrophotomètre UV-visible par absorption sur solution (DMSO) ou après séparation par chromatographie liquide. L'emploi d'un système informatisé permet d'opérer par dérivées multiples du spectre jusqu'au 6ème ordre. L'emploi de fibre optique permettra, par réflexion, d'identifier les colorants directement sur la peinture (11).

### 4) Nouvelles applications ou développement de techniques d'examen

Micheli Mario, (Italie : Rome, Istituto Centrale del restauro)

En complément à l'examen thermographique, radiologique et ultrasonique, l'endoscopie permet une inspection directe de l'intérieur des objets. Le boroscope puis les fibres optiques sont maintenant assortis de téléobjectifs, autofocus, de détecteurs vidéo (2mm de diamètre, 51000 pixels) avec moniteur et enregistreur. La mise au point d'un télémanipulateur sous contrôle optique va permettre d'effectuer des prélèvements de noyaux dans les bronzes.

Kristev Krassimir, (Bulgarie : Sofia)

L'utilisation d'une caméra de thermovision AGA 750 a permis, après chauffage modéré d'une icône partiellement dévernée, d'une copie d'icône et des témoins de couleurs, de constater l'inertie thermique de chacun des objets. La périphérie et les zones dorées sont plus froides. Les parties non dévernées se refroidissent plus lentement de même que le noir d'os et la malachite.

George Wechsung, Randell Evans, James Walker, Maryan Ainsworth and Gary W Carriveau, (USA)

Une collaboration scientifique entre le Metropolitan Museum of Art, la National Gallery of Art et l'Amparo Corporation a permis de résoudre, au moyen de l'ordinateur, le problème de l'assemblage des prises de vues digitales obtenues par reflectographie infra-rouge. Le système effectue le stockage des images, la correction des distorsions de la caméra et le traitement de l'image. La qualité du résultat est incomparable aux montages mosaïques de clichés photographiques.

Sadatoshi Miura, (Japon : Tokyo, National Research Institute of Cultural Properties)

L'investigation scientifique du temple Kakurinji Kakoganta par refléctographie infra-rouge et émissiographie a permis de retrouver sur quatre colonnes du hall consacré au Prince Shotoku (1112 AD) des dessins originaux quasi illisibles représentant Acala, Kinkara et Cetaka.

Achim Unger, (RDA : Berlin, Staatliche Museen)

La consolidation d'un cadre de peinture baroque au moyen de méthacrylate de méthyl a été contrôlée par rayonnement X. La tomographie par rayons X a permis d'apprécier quantitativement dans la masse à partir de plans de coupes repartis régulièrement le degré d'altération du sapin puis l'hétérogénéité de pénétration du méthacrylate de méthyl.

Les radiographies de plans de coupes radiales peuvent également servir à l'examen dendrochronologique.

John M Taylor, Ian N M Wainwright, F R Livingstone, M Rioux, P Boulanger, (Canada : Ottawa, Canadian Conservation Institute)

Le scanner 3D à laser (10mW hélium-néon) développé par le National Research Council of Canada permet d'effectuer le relevé rapide et non destructif du relief d'objets de formes complexes pour la documentation, la production de copies mais également la recherche en conservation. La mesure de la variation dimensionnelle d'un objet après restauration, ou en cours d'exposition, peut être utile à la préservation de pièces fragiles. La vitesse de saisie dépend du niveau de définition désiré.

#### 5) Nouvelles application ou développement de techniques d'analyse

Giorgio Accardo, (Italie : Rome, Istituto Centrale del Restauro)

Giovanni Santucci, (Italie : Rome, Université)

La restauration structurale de la statue équestre de Marcus Aurelius nécessite d'en connaître la résistance mécanique. Après avoir déterminé son état de conservation (distribution de l'épaisseur du métal, localisation des défauts, des joints d'assemblage et la composition des alliages constitutifs), la cartographie des contraintes subies par le métal du cheval supportant le poids du cavalier (620 kg) a été établie à partir d'un modèle réduit (1/5) en bronze coulé à la cire perdue et réalisé à partir de relevés photogrammétriques. L'application sur le modèle de jauges de contraintes aux zones de déformation a permis de déterminer d'une manière non destructive le mode de consolidation approprié.

M C Papillon, R Lefevre, Ch Lahanier, A Duval, J P Rioux (France : Paris, Université de Créteil - LRMF)

La préparation au microtome d'échantillons de peinture de chevalet sous forme de coupes ultra-fines (100nm) transparentes aux électrons accélérés d'un microscope électronique à transmission permet d'identifier individuellement chaque pigment à partir de sa composition élémentaire (émission X) mais également structurale (diffraction d'électrons). L'identification peut être généralisée à partir de la forme et de la taille des grains liées à la nature et au mode de fabrication des pigments visibles sur l'image des électrons transmis (X40 000).

A Kossolapov, (URSS : Leningrad Hermitage Museum)

L'étude des peintures de chevalet impose souvent d'opérer sans prélèvement. L'analyse élémentaire de surface du tableau effectuée par microfluorescence X nécessite d'interpréter les résultats pour caractériser les pigments. La mise au point d'une chambre de diffraction X à focalisation permet leur identification in situ sur des surfaces planes inférieures à 16mm<sup>2</sup> (8 x 2mm<sup>2</sup>).

Masako Koyano et Takeo Kadokura, (Japon : Tokyo National Research Institute for Cultural Properties)

L'apparition de cristaux à la surface et dans la couche picturale de quatre peintures japonaises du deuxième quart du 20ème siècle a nécessité une expertise scientifique. La mise au point d'un diffractomètre X spécial a permis d'analyser directement la couche picturale et d'identifier du sulfate de zinc hydraté issu de la transformation de l'oxyde de zinc situé dans la préparation en présence d'atmosphère humide et polluée.



Marta Jaro, Laszlo Kriston et Agnes Timar-Balazoy, (Hongrie : Budapest, Centre National des Musées)

Les tissus imprimés médiévaux européens sont rares. Des 120 échantillons analysés par King en 1962, seuls 40 pièces se sont révélées authentiques. 6 fragments des plus anciens tissus imprimés du 13ème au 15ème siècle conservés au Musée de Budapest ont été analysés par diffraction X. La présence de sulfate de baryum, associé aux pigments rouges et verts peut paraître surprenante; de même que celle de cuivre et d'étain à la place d'or et d'argent.

Don Robins, Grande Bretagne : Londres, Université

L'analyse de prélèvements de 30mg de sceaux royaux en cire verte (acétate de cuivre) noire, rouge (sulfure de mercure, ou jaune (oxyde de plomb), tout d'abord par diffraction X puis par spectrométrie de résonance magnétique nucléaire à transformée de Fourier Cl3 montre une évolution chronologique de composition : cire d'abeille au moyen âge, puis mélange de résine de pin (colophane) et de cire d'abeille jusqu'au règne de Georges III. La cire minérale remplace ensuite la cire d'abeille. Le changement d'aspect de certains sceaux est attribuable à une modification physique plutôt que chimique.

You Sun Kim, (Corée : Chung-Nam Advanced Energy Research Institute)

L'application de méthodes spectroscopiques d'analyse : (absorption atomique, activation neutronique, émission UV visible avec source plasma) a permis de caractériser finement jusqu'aux éléments en traces la composition de divers matériaux : pièces de monnaies chinoises en bronze, originales et d'imitation, verres, laitons et porcelaines antiques.

Jiri Cejka, Ivana Cejkova et Zdenek Urbance, (Tchékoslovaquie : Prague, Musée National)

L'analyse de 52 échantillons de produits de corrosion prélevés sur 24 objets en bronze conservés au Musée National de Prague par diffraction X et spectrométrie infra-rouge montre que, malgré la situation du musée en atmosphère citadine fortement polluée, les altérations du métal sont celles qui se sont formées dans le sol et ne proviennent pas des polluants de l'air SO<sub>2</sub> et NO<sub>x</sub>.

Mirella Simonetti : (Italie, Bologna)

Les microtests de solubilisation de vernis lors de la restauration de l'Annonciation de Gerolamo Genga (1520) conservée dans l'église San Agostino à Cesena révèlent qu'aucun solvant ne convient pour cette restauration sans altérer aucune couche picturale.

Ces divers travaux n'illustrent, bien sur, qu'une partie des activités de recherche menées sur les oeuvres d'art mais témoignent de l'effort accompli durant ces trois années pour intégrer les techniques scientifiques dans le domaine de la conservation. Il me semble utile d'associer à cet article deux communications récentes qui font également preuve de nouveautés : l'application de la résonance paramagnétique électronique à la caractérisation du jay (12) et l'analyse globale de verre et de glaçures excités sous faisceau de muons (13). D'autres techniques restent à explorer pour accroître le rôle privilégié des méthodes non destructives au sein des musées. Ce sera l'un des objectifs permanent de notre programme.

Toutefois simultanément à cette avancée technologique il me semble également nécessaire durant la prochaine période triennale d'engager des synthèses, d'effectuer des bilans, dans quelques domaines que nous aurons à définir, au moyen d'enquêtes menées au niveau mondial et de tables rondes thématiques. L'un de ces thèmes pourrait concerner la typologie des altérations de peintures de chevalet proposé par Madame Perier d'Ieteren.

Mes remerciements s'adressent collectivement aux coordonnateurs adjoints et membres actifs qui ont accepté de consacrer de leur temps pour faire progresser la Connaissance. Je nourri l'espoir que cette amicale collaboration suscite encore de nouveaux développements scientifiques voués à la conservation du patrimoine mondial.

BIBLIOGRAPHIE

- (1) Drilhon F., Laval-Jeantet M., "Reconstitution tridimensionnelle de "calculi" mésopotamiens", Preprints 7th Triennial Meeting ICOM-CC, Copenhagen, 10 - 14 septembre (1984) pp 84.1.62 - 85.1.64
- (2) M. Marabelli Appociazione Italiane prove non distruttive Istituto Centrale per il restauro eds., "Proceedings of the First International Conference on non destructive testing in conservation of works of art", Roma 27-29 octobre 1983
- (3) Zucker A. eds., Oak Ridge National Laboratory, Numéro spécial consacré à l'étude des oeuvres d'art par faisceau d'ions accélérés., Ion Beam Techniques in Archaeology and the arts. Nuclear Science Applications, Section B, volume 1, number 5, 1983
- (4) Andersen H.H. et Picraux S.T. eds., Ion Beam Analysis in the Arts and Archaeology, Nuclear Instruments and Methods in Physics Research, Section B, volume B14, N°1, North-Holland, Amsterdam, janvier 1986.
- (5) Furlan G., Cassola Guida P., Tuniz C., eds., New paths in the use of Nuclear Techniques for Art and Archaeology, International Society of Science and Art, Trieste Italy, 30 septembre - 3 octobre 1985.
- (6) Riflettoscopia All'Infrarosso computerizzato. Quaderni N°6 Ministero per i Beni Culturali e ambientali, Venezia 1984.
- (7) Van Schoute, Colloque VII pour l'étude du dessin sous-jacent dans la peinture: géographie et chronologie du dessin sous-jacent. Leuven, Louvain-la-Neuve, France, 17-19 septembre 1987.
- (8) Symposium Zerstörungsfreie Prüfung von Kunstwerken, Berlin Dahlem 8 und 9 october (1987)
- (9) "Scientific investigations of Raffaello's paintings", proceedings of the meeting organised by the Politecnico di Milano and the Soprintendenze per i Beni Artistica e Storia della Lombardia Occidentale, 26-28 June 1986.
- (10) Ministère de la Communauté française de Belgique eds., "Watteau : Technique picturale et problèmes de restauration", Catalogue, Université Libre de Bruxelles, 22 November - 12 December 1986.
- (11) Proceedings of the Congress Euroanalysis VI, Paris, September 7-11 (1987)
- (12) Sales K.D., Oduwoles A.D., Couvert J. and Robins G.V., Identification of jet and related black material with ESR, Archaeometry 29,1 (1987), p.103-109
- (13) Daniel H., Hartmann F.J., Köhler E., Beitat U., "Application of muonic X rays in Archaeology", Archaeometry 29, 1 (1987) p110-119.



## SUMMARY

Piero della Francesca's paintings after the middle of the 15th century show a remarkable affinity to Netherlandish painting not only in stylistic and iconographical features but also in painting techniques. His study of Eyckian painting, knowledge of van der Weyden's art and working side by side in Urbino with Joos van Ghent stimulated a growing interest to experiment with northern techniques.

On the occasion of the restoration of the Sacra Conversazione painted in the last quarter of the 15th century (Milan, Brera), a few samples were taken from the panel, the supporting canvas, the ground and the paint layer and analyzed by various laboratory methods.

The results of this study have shown specific traits of Piero's later technique and style. Some data is compared to results of studies carried out on Flemish paintings (van Eyck - Joos van Ghent).



Fig. 1 x-ray photograph, detail of the Virgin.

# A STUDY OF PIERO DELLA FRANCESCA'S SACRA CONVERSAZIONE AND ITS RELATIONSHIP TO FLEMISH PAINTING TECHNIQUES

Ingrid C. Alexander  
314 Southside Avenue  
Freeport, L.I. New York 11520  
USA

Antonietta Gallone Galassi  
Istituto di Fisica del Politecnico  
piazza Leonardo da Vinci, 32  
20121 Milano  
Italia

## Introduction

Piero della Francesca's late style demonstrates a growing interest in the subtleties of light and color and reveals a meticulous analytical study of surface textures. The commission from Federico da Montefeltro to paint the Sacra Conversazione came at a time when Piero was fascinated by Netherlandish style. His research is a technical as well as an iconographical one. The Count's scintillating armor, the luminous jewels on the heads of the angels and the rich red carpet below the Madonna's feet reflect an almost Eyckian world. An x-ray photograph of the Virgin shows that Piero originally intended to paint a large jewel on her forehead but in the final execution of the painting decided to paint out this detail (Fig. 1).

The northern theme of representing the Madonna in an ecclesiastical setting may have been suggested to him. The architectural elements of the church envelope the figures and continues beyond the picture plane much in the way it does in the van der Paele Madonna painting by van Eyck. While the composition is Netherlandish in inspiration and frequently found north of the Alps, in Piero's panel it is the first time the theme is represented in Italy on such a monumental scale.

It is known that Federico da Montefeltro was a great patron of the arts and particularly drawn to Flemish painting. As Vespasiano da Bisticci, a friend and historian, recounts, he sent to Flanders for a painter who could paint in oil.

When Joos van Ghent arrives in Urbino to paint the Communion of the Apostles and decorate the studiolo of the palace; Piero was working on the large panel (248 cm x 170 cm). Piero and Joos worked side by side at the court of Urbino where they were able to exchange ideas on materials and technique.

For decades, authors have written a great deal concerning who painted or repainted the hands of the Count in the panel as we see them today - whether Pedro Berruguete or Joos van Ghent. Though there is general agreement that the artist is non-Italian, the authorship is still in question. This study has been able to determine that Montefeltro's praying hands are repainted.

On the occasion of the restoration of the panel - Carlo Bertelli, director; Pinin Brambilla Barcillon, restorer - a few samples were taken from the wood, the canvas support and from the paint layer. The samples were examined with the following analytical techniques: observations with the optical microscope Leitz Ortholux and the electronic microscope, EDS Stereoscan 150 Cambridge, microchemical tests, staining tests, x-ray fluorescence with electron microprobe EDS Link 860 and microspectrofluorometric analysis on cross-sections with U.V. source.

## Results and Comments

### The Support

The altarpiece is painted on poplar (*populus alba*) over which a red-stained (*rubia tinctorum*) linen canvas was found. This canvas may be a fragment of a standard that was used in place of the traditional white linen that is customarily placed between the wooden panel and the gesso ground. Cennino Cennini's treatise on painting describes studio practices at the time and how an old white canvas should be chosen to place over the panel. Piero's choice of a red canvas may have answered his desire for a warm chromatic underpaint. A significant departure from the green underpainting visible in his earlier paintings.

### The Ground

Above the red-stained canvas, a preparatory layer of gesso



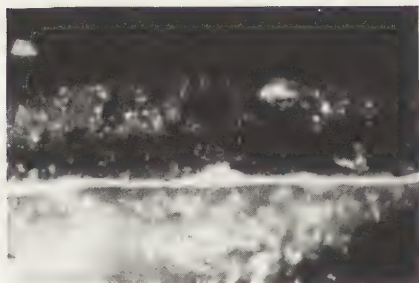


Fig. 2 microphotograph of cross-section of a sample from the green panel of marble on the right of the niche

1. gesso ground + animal glue
2. thin lead white underpaint
3. a brown resinous material
4. copper resinate layer

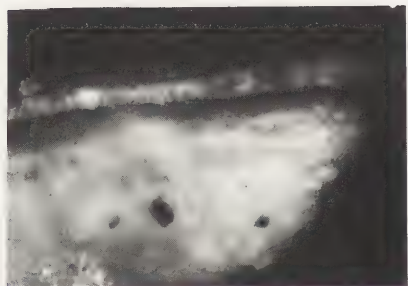


Fig. 3 microphotograph of cross-section of sample of red from angel's mantle

1. gesso ground + animal glue
2. thin layer of animal glue
3. vermilion + lead white, some large particles of red lake
4. thin layer of red lake glaze

(calcium sulfate) with traces of aluminum and potassium silicates bound with animal glue were identified. Paintings in the north were invariably executed on oak panels prepared with a chalk (calcium carbonate) ground combined with animal glue. Of course, Joos van Ghent chose the materials available to him when he worked in Urbino - poplar panel and gesso for the ground.

#### Pigment and Paint Layer Structure

The following pigments were identified: natural ultramarine, azurite, smalt, copper resinate, vermilion, red lake, yellow and red ochre, carbon black and lead white.

Between the ground and the paint layer a thin application of animal glue is visible in some areas. In certain cases, a thin layer of lead white ( $\sim 5\mu$ ) is noticeable underneath the paint layer: the grey entablature, the red of the porphyry fillet, the green of the square of marble from the architecture in the background and in the blue under the green of St. Andrew's robe. A thicker layer ( $\sim 20\mu$ ) of resinous material is present under the color of the floor. Under the green copper resinate (a marble panel, the robes of the saints) both layers are observed: lead white and a resinous brown, one above the other.

The thickness of the paint layer is between 20 - 30  $\mu$ . The pigments are always mixed with white lead.

#### Blue

In samples taken from the Madonna's mantle, natural ultramarine (lapis-lazuli) can be seen over a layer of azurite. Azurite was also identified in the marble of the architecture in the cloak of St. John the Baptist and in the layer just below the green robe of St. Andrew. Small particles of smalt were observed in the light blue of the floor. Smalt, a blue pigment made from the grinding of glass, is usually not found in Early Netherlandish painting. In the 15th century the paint structure in the Netherlandish school was built up of superimposed thin layers. Van Eyck's Adoration of the Mystical Lamb demonstrates a complex system of layers. In samples of blue from the Madonna's cloak, two layers of lapis-lazuli (some lead white is present in the lower one; the upper one is a glaze) are above two layers of azurite and lead white. Joos van Ghent's technique reveals a simpler structure of fewer layers.

#### Green

Copper resinate was identified over a thin layer of azurite in a sample taken from the robe of St. Andrew. It was also found as a translucent glaze over the brown resinous material extended over the ground in a sample from a panel of marble in the niche (Fig. 2). Its use corresponds to the traditional manner that Cennini recommends in using it as a glaze. Transparent lakes are much in use by artists in Italy of this period. In Flanders, in order to achieve the beautiful deep greens so characteristic of this school of painting, several layers of green paint are used. Generally they are composed of malachite and lead white with the occasional addition of an organic yellow for warmer tones and then glazed with copper resinate.

An unusual technique is observed in Joos van Ghent's Communion of the Apostles. A layer comprised of malachite and lead white, at times with a little ochre, is found to be above a translucent layer of copper resinate containing a few grains of malachite. A rare example of a glaze situated below an opaque layer.

#### Red

A sample taken from the porphyry fillet of the architecture contains vermilion and carbon black. Large particles of red lake are found in the mantle of an angel (Fig. 3) and red lake with large amounts of lead white are in St. Andrew's mantle. Transparent lakes are present as glazes here and in the angel's mantle. Similar structures are found in paintings in the north: vermilion and lead white, glazed with a red lake. When the tones approach purple, particles of lapis or azurite are introduced.

#### Grey

Carbon black and lead white were found in a sample of the broad entablature of the architecture. Lead white dominates here and its presence in the underpainting also contributes to the luminosity of this area.



### Skin Tones

The skin tones of St. Andrew are composed of lead white with a few particles of vermilion, red lake, red and yellow ochre, copper resinate, carbon black and smalt.

The sample taken from the hands of Federico shows two layers of color separated by an organic layer based on a drying oil (Fig.4). The layer directly above the ground is similar in composition and thickness to those described above. The uppermost layer is thinner, probably an overpaint, and more pink. It is composed of lead white with a little vermilion.

Flesh tones in Flanders were also painted in one layer and based also on lead white and vermilion. Joos van Ghent varies his technique used in the Calvary altarpiece (St. Bavo, Ghent) when he arrives in Urbino. There he uses lead white, bone black and vermilion, red lake and sometimes a little malachite make up the skin tones.

### Binding Media

The identification of the medium of the Montefeltro altarpiece was carried out with microchemical tests (1,2) and more recently with microspectrofluorometric analysis with U.V. source ( $\lambda = 366 \text{ nm}$ ) (3) that delivers a spectrum of fluorescence, layer by layer. In addition, microphotographs were taken of cross-sections in ultraviolet light ( $\lambda = 366 \text{ nm}$ ).

The results of the analytical techniques show the following: Animal glue is present in the ground. Egg is present in all the colors with the exception of the grey entablature, the blue of the marble and the skin tones, where oil is the medium. It cannot be excluded that in the original flesh tones a protein is present. A resinous medium is present in the blue mantle of St. John the Baptist as well as an underpaint of the floor and the transparent greens of the robes of the saints.

### Conclusion

Piero painted the greater part of the altarpiece using the traditional egg tempera technique. However, the painting also shows some variation of this technique. As expected, there is a thin layer of lead white between the ground and the paint layer. Traditional too and described by Cennini, are the red lake glazes over a vermilion and lead white base. Azurite is sometimes added to obtain a blue tone. Natural ultramarine (lapis-lazuli), a very precious pigment, is to be found in the Virgin's robe. Its use is usually reserved for important commissions and it appears to have been even costlier in the north. In Flanders when natural ultramarine is found in the paint layer it is usually associated with an aqueous tempera medium. Piero's colors are well-defined and generally made up of one pigment, rarely with traces of other colors. Though skin tones are composed of lead white together with small quantities of various pigments. The opaque and rather undistinguished malachite is abandoned in the large ample zones of the robes. In these areas, the chosen green is the beautiful copper resinate to which a brown undercolor provides greater depth of tone (4).

With regard to the binding medium identified in the panel, egg was found to be the medium in the Virgin's mantle (natural ultramarine). Azurite found in the light blue of the marble is bound with oil. A drying oil is also found in the grey color of the entablature of the background and in the skin tones. In Italy at this time, flesh tones are usually carried out in a tempera medium. Piero modifies traditional methods to achieve a more luminous visual effect. Unexpectedly, a brown resinous binding medium was discovered in the darker blue (azurite) of the mantle of St. John the Baptist. Azurite is often found coarsely ground in paintings in order to intensify the color since it is somewhat transparent. The larger crystals require a great quantity of binding medium. The premature cracking that is seen in this panel and others painted in the same period and later is probably due to an excess of oil, resin or oil/resin mixture with regard to the pigment particles. Piero was apparently not yet quite familiar with this new technique of painting with oils and still experimenting with it.

A very dark layer of a resinous substance is present as a base tone in the light variegated colors of the floor. Oil is also observed, probably in the flesh tones (tempera grassa - a technique lying somewhere between oil and tempera). A drying oil alone in the architectural background would seem to indicate a

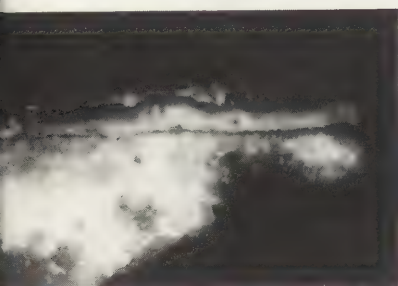


Fig. 4 microphotograph of cross-section of sample from Federico's hands

1. gesso ground + animal glue
2. very thin layer of animal glue
3. lead white + rare particles of vermilion, copper resinate, carbon black, red and yellow ochre
4. layer of drying oil
5. a pink layer of lead white + vermilion

departure from traditional techniques.

In Flanders, the luminous enamel-like surfaces were achieved by superimposing thin layers of color on a brilliant chalk ground. Analysis has shown the binding media to be a complex system. Pigments are found to be bound in an aqueous tempera medium (generally reserved for natural ultramarine and the bone black of the underdrawing), an emulsion (tempera grassa, oil + protein), a drying oil and a drying oil with the addition of an unknown substance, x, which may be a resin.

In Italy, oil was first used as glazes. Its introduction into the paint payer was a gradual process and it was used more systematically in the last quarter of the 15th century. Piero della Francesca appears to be a major protagonist in adopting these new methods with a keen interest in experimenting with them. The last part of his life is dominated by an intense study of the iconographical and technical features of Early Netherlandish painting. Interest in these methods were noted already by Cennino Cennini who wrote "... ti voglio insegnare a lavorare d'olio in muro o in tavola, che l'usano molto i tedeschi..." (5).

#### Notes and References

1. DIMOS, ICR, I,I, Tecniche di esecuzione dei materiali costitutivi, Roma, 1978.
2. E. Martin, "Some Improvement of Analysis of Paint Media," *Studies in Conservation*, 22, 1977, pp. 63-67.
3. E. Bernacchi, G. Bottiroli, A. Gallone, "Microspectrofluorometric Techniques as Applied to the Analysis of Binding Media and Varnishes in Colour Samples Taken from Paintings," *Scientific Methodologies Applied to Works of Art*, Atti del Convegno, Firenze, 2-5 maggio, 1984, pp. 168-70.
4. The greens are executed in an analogous way in later works that we are studying: "Padreterno" by Pietro Perugino (Cortosa di Pavia), "Lo Sposalizio della Vergine" by Raffaello (Brera, Milano).
5. Cennino Cennini, "Il Libro dell'arte", ed. by Neir Pozza, Vicenza, 1971, Cap. LXXXIX, p. 97.
6. Jacques Lavalleye, "Le Palais Ducal d'Urbino", *Les Primitifs Flamands. Corpus de la Peinture des Anciens Pays-Bas*, I, 7, Brussels, 1964.
7. Millard Meiss, "La Sacra Conversazione di Piero della Francesca", *Quaderni di Brera*, 1971.
8. P. Coremans, R.J. Gettens, J. Thissen, "La technique des Primitifs flamands," *Studies in Conservation*, vol. I, 1952, pp. 1-29.
9. Paul Coremans, "La technique des Primitifs flamands. Van Eyck: L'Adoration de l'Agneau Mystique," *Studies in Conservation*, vol. I, 1954, pp. 145-161.
10. L. Kockaert and M. Verrier, "Application des Colorations A L'Identification des Liants de Van Eyck," *Bulletin de L'Institut Royal du Patrimoine Artistique*, XVII, 1978-79, pp. 122-127.
11. P. Brinkman, L. Kockaert, L. Maes, L. Masschelein-Kleiner, F. Robaszynski and E. Thielen, "Het Lam Godsretabel van Van Eyck. Een Heronderzoek naar de Materialen en Schildermethoden. 1. De Plamuur, De Isolatielaag, De Tekening en De Grondtonen." *Bulletin de L'Institut Royal du Patrimoine Artistique*, XX, 1984-85, pp. 137-166.



## RESUME

Nous présentons ici une première esquisse de classification des différents types d'altération. Trois grandes familles de causes ont été prises en considération, le temps (patine au sens large), la technique d'exécution (matériaux et mise en oeuvre) et le nettoyage des peintures (degré d'intervention). Ces causes changent, plus ou moins profondément, certains caractères de la couche picturale, notamment son état de surface et modifient donc la perception de l'image.

## TYPOLOGIE DES ALTERATIONS DE SURFACE DE LA COUCHE PICTURALE

Ségolène BERGEON

Conservateur, chef du Service de Restauration des peintures des Musées Nationaux  
Petites Ecuries du Roy  
Avenue Rockefeller  
78000 VERSAILLES

Catheline PERIER-D'ETEREN

Chargée de Cours  
Université Libre de Bruxelles  
Section Histoire de l'art (CP 175)  
Avenue Franklin Roosevelt, 50  
1050 BRUXELLES

Préliminaires

Au sein du groupe de travail Investigation scientifique des peintures, il a paru intéressant de se pencher sur l'élaboration d'une méthode d'examen et d'une documentation photographique rigoureuse qui permettent d'apprécier l'état de conservation des surfaces picturales. En effet, les altérations de surface, dues à la technique d'exécution, à la restauration et/ou au nettoyage, provoquent des désaccords au sein de la structure formelle de l'image qu'il faudrait impérativement relever de façon méthodique.

L'interruption anormale d'un modelé, la situation inadéquate d'un ton qui avance au lieu de suggérer une profondeur, l'agressivité matérielle de certaines couleurs qui affleurent hors du milieu spatial de la peinture pour se présenter directement comme matière, faussent la lecture de l'image et, par conséquent, sa juste appréciation stylistique. Il conviendrait donc, de s'interroger sur les causes des dégradations ou des désaccords observés qui, sans être nécessairement le résultat de la dernière intervention ou du dernier nettoyage, ont été mis en évidence par ceux-ci.

Cette constitution d'une documentation photographique de référence qui étendrait l'examen traditionnel de contrôle stratigraphique de la couche picturale à un examen de ses états de surface, doit se faire à un niveau international. Elle requiert, en effet, une adaptation spécifique qui doit être expérimentée sur le plus grand nombre de cas possible afin d'être à même de fixer, de transmettre et de comparer les relations observées entre l'effet esthétique de la peinture et son support matériel.

Notre apport sur la typologie des altérations de surface de la couche picturale vise à fournir les premières données nécessaires à l'élaboration de cette méthode d'examen.

Nous aimerions que les observations que nous y avons rassemblées soient complétées ou précisées par un travail interdisciplinaire qui pourrait déboucher dans une deuxième phase sur l'exploitation de ces données : pour réaliser et décrire les conséquences optiques des accidents de surface relevés et partant, essayer de définir une méthodologie de la restauration et/ou du nettoyage qui, tout en restituant aux peintures une lisibilité optimale leur éviterait, à l'avenir, d'être soumises à des modifications irréversibles. Cette démarche nous paraît être, comme l'écrivait Paul Philippot, la condition de tout dialogue réellement scientifique.

## I. VERNIS

1. Dépôt de poussières.
2. Dépôt de poussière grasse = crasse.
3. Faïençage = microcraquelure d'âge; réseau spécifique au vernis, localisé dans celui-ci, dû aux mouvements du support dont les effets peuvent être particuliers sur une couche rigide.
4. Craquelures d'âge = réseau de craquelures dû aux mouvements du support qui entraînent des ruptures de la préparation et des couches de couleur.
5. Craquelures prématurées = craquelures ou microcraquelures limitées aux couches de vernis et dues à un mauvais séchage de celui-ci.
6. Variété d'assombrissement du vernis en fonction des critères suivant :
  - nature de la résine (ex. : la gomme laque roussit);
  - Adjuvants (ex. : siccatifs au manganèse);
  - diffusion d'éléments contenus dans les couches sous-jacentes (ex. : protéines, pigments).
 La variation de couleur peut être jaunâtre ou tirer vers le roux (gomme laque) ou le noir (manganèse).
7. Vernis (ou autre couche) coloré.
8. Surface grisâtre (patine : effet exclusivement dû au temps ou couche voulue).
9. Bleuissement = condensation locale d'humidité qui provoque une diffusion de la lumière.

10. Chanci = blanchiment ou opacification du vernis par perte de substance de celui-ci (dissolution chimique, dans l'eau) et microfissuration du film continu.
11. Matité = distribution irrégulière due :
  - à une absorption irrégulière = embu (la matité correspond à une forme sous-jacente);
  - à une pose irrégulière (ex. : traces de brosse visibles).
12. Brulûre = la chaleur a causé un grésillement du vernis et a provoqué la formation de microbulles plus ou moins éclatées.
13. Déplacage = lacune du vernis.
14. Coulure = épaisseur irrégulière décelable par un assombrissement dans la zone la plus épaisse.
15. Influence de la texture sur la distribution du vernis :
  - selon la technique d'exécution de la peinture : empâtements;
  - selon le support : support de toile
    - type du tissage (armure toile, sergée, damassée);
    - tissages irréguliers;
    - tissage lâche : structure pavimenteuse de la peinture;
    - "guirlandes" : effet dû à la tension de la toile.
  - support de bois
    - fil marqué du chêne : sombre;
    - cernes plus ou moins réguliers des résineux.
16. Épaisseur du vernis.

## II. COUCHE PICTURALE

Seront prises en compte ici toutes les altérations de la couche picturale (1) y compris celles qui sont induites par des altérations de la préparation dans la mesure où elles ont une incidence optique.

1. Perte d'exsudat = perte de la couche superficielle de liant recouvrant la couche formée de liant et de pigment; cette perte entraîne la modification des conditions de réflexion de la lumière (on passe de la réflexion de type métallique à la réflexion diffuse) et par conséquence la diminution de la profondeur de ton (couleur "lavée" de blanc).
2. Perte de glacis :
  - usure du glacis ou "épidermage", c'est-à-dire perte de glacis :
    - sur les reliefs de la texture
    - sur la crête des empâtements;
  - élargissement optique du réseau de craquelures d'âge, c'est-à-dire perte de glacis sur les bords relevés de la matière le long des craquelures;
  - perte locale = lacune.
3. Perte de la couche de couleur proprement dite :
  - usure ou épidermage, c'est-à-dire perte de couleur :
    - sur les reliefs dus à la texture du support
    - sur les reliefs dus à la préparation
  - élargissement optique du réseau de craquelures d'âge, c'est-à-dire perte de la couleur sur les bords de la matière le long des craquelures;
  - perte locale = lacune, entraînant une perte complète de la forme ou partielle de son contour;
  - dédoublement c'est-à-dire perte d'adhérence entre deux couches de couleurs, ou entre la préparation et la couche de couleur, ayant provoqué une chute de matière.
4. Perte de préparation = lacune profonde :
  - profondeur limitée (inférieure à l'épaisseur de la préparation);
  - complète : jusqu'à voir le support.
5. Transparence accrue rendant visible :
  - un repentir de forme au niveau de la sous-couche ou un ton de fond.
  - la préparation (colorée ou non);
  - le support (ex. : maille du chêne, coloration du cuivre, ...).
6. Opacification du glacis :
  - soit par fissuration du liant;
  - soit par décoloration d'un pigment (certaines laques rouges et la laque jaune brunâtre dite "stil de grain" deviennent jaunâtres et translucides; l'outremer peut blanchir; le smalt devient translucide et blanc-jaunâtre).
7. Modifications chromatiques des couches de couleur proprement dite en fonction :
  - des transformations de couleur de pigment (laques rouges et jaunes; certains verts de cuivre roussissent; l'argent noircit);
  - des transformations de couleur du liant (ex. : une couche bleue azurite devient apparemment moire par brunissement du liant interstitiel).
8. Jaunissement du liant : l'huile non exposée à la lumière jaunit (phénomène réversible). Une reprise d'auteur (repentir) est dite : "plomber".
9. Diffusion d'une couleur dans une autre.
10. Plissements.
11. Aplatissement :
  - général (un retoilage risque d'accentuer l'effet de texture dû à la toile originale) : texture "pavimenteuse"  
texture serrée du "tuchlein"



- type du tissage (armure toile, sergée, croisée ou damassée  
tissage irrégulier (fils plus ou moins gros);
- local (arasement de la crête des empâtements);
  - effet de fossé (en creux) autour d'un empâtement enfoncé.
12. Relief irrégulier lié aux craquelures :
- écailles en "tuile" (la matière picturale est relevée le long des craquelures).
  - soulèvement (stage ultérieur par rapport au paragraphe ci-dessus, avec déjà des micropertes au croisement de deux craquelures).
13. Brûlures :
- grésillement : (fusion du liant et formation de microbulles plus ou moins éclatées);
  - cloque;
  - changement de couleur (soit du pigment, par exemple un oxyde ferreux vert devient un oxyde ferrique rouge; soit du liant qui brunit).
14. Craquelures d'âge :
- en fonction du support :
    - réseau irrégulier (toile);
    - réseau à direction privilégié général (bois);
    - réseau local à direction privilégiée.
15. Craquelures prématurées :
- plus ou moins profondes;
  - jusqu'à voir la préparation (gerçure ou crevasse).

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#### Note 1

On notera que le terme de couche picturale revêt une signification différente en France et en Belgique.

#### Schéma d'une structure stratifiée : présentation type en Belgique

- A. Support
- B. Préparation
- C. Couche picturale soit sous-couches de couleur et glacis
- D. Couche de protection soit vernis

#### Références :

P. Coremans, l'Agneau Mystique au laboratoire. Examen et traitement, Bruxelles, 1953, p. 17. et C. Périer-D'Ieteren, Colyn de Coter et la technique picturale des Primitifs Flamands du XVe siècle, Bruxelles, 1985, fig. 1b.

#### Schéma d'une structure stratifiée : présentation type en France (SRPMN)

- A. Support
- B. Couche picturale :
  1. encollage
  2. préparation
  3. couche colorée (couche de couleur proprement dite et glacis)
  4. vernis.

#### Références :

Gilberte Emile Mâle, Restauration des Peintures de chevalet, Fribourg, Office du livre, 1976, p. 41 et S. Bergeon, Restauration des Peintures, Dossier du Département des Peintures n°21, Paris, Réunion des Musées Nationaux, 1980 (schéma p. 15).





## SUMMARY

X-ray powder diffraction and infrared spectroscopy were shown to be suitable analytical methods for determining corrosion products (patinas) on prehistoric and antique bronze artifacts obtained from archaeological excavations and deposited in the National Museum in Prague. An analysis of patina composition demonstrates that the high concentrations of harmful air pollutants (especially  $\text{SO}_2$  and  $\text{NO}_x$ ) in the area where the museum is located have not contributed to the corrosion of the artifacts. Instead, the corrosion products composition conforms to that formed during soil deposition.

# CONTRIBUTION TO THE STUDY OF THE EFFECTS OF THE ENVIRONMENT ON ANCIENT BRONZE ARTIFACTS USING THE X-RAY POWDER DIFFRACTION AND INFRARED SPECTROSCOPY

Jiří Čejka and Ivana Čejková

National Museum in Prague, Research Chemistry Division, Vítězného února 74, 115 79 Praha 1, Czechoslovakia

Zdeněk Urbanec

Nuclear Research Institute, 250 68 Řež, Czechoslovakia

## Introduction

When climatic conditions (temperature and relative humidity) are not favorable, bronze artifacts deposited in museums and depositories can be exposed to harmful effects of air pollutants, especially  $\text{SO}_2$  and  $\text{NO}_x$ . These air pollutants can cause a set of corrosion products and deposits that can ultimately bring about a complete destruction of the artifact (CCI Note 9/1, 1986). Approximately fifty corrosion products and deposits have been found on bronze artifacts exposed to the outdoors (Riederer, 1985). Because of the increasing concentrations of  $\text{SO}_2$  and  $\text{NO}_x$  in the air, we would expect to find this type of corrosion product on bronze artifacts inside of museums. The corrosion process would occur at the copper oxide layer in the presence of high humidity and  $\text{SO}_2$  and  $\text{NO}_x$  in the air, or by action of these pollutants on previous corrosion products (especially malachite) produced during burial conditions. We would especially expect to find hydroxosulphates of the brochantite and antlerite types. If these compounds are not present in the corrosion products, it follows that air pollutants are not the cause of the corrosion. In examining this question, however, it is necessary to consider the corrosive effects of organic acids produced by the decomposition and oxidation of various polymeric materials (lacquers, varnishes, adhesives, binders) used in museums. The use of such materials - and the corrosion caused by them - has become common place in recent years (Riederer, 1979, 1981).

We based our study on the collection of prehistoric and antique bronze artifacts deposited in the National Museum in Prague. These artifacts, obtained from archaeological excavations (e.g. Sakař, 1970) have not been conserved. The curators of these collections consider these artifacts to be in danger of deterioration. There are two possible explanations for the corrosion products on these artifacts: soil corrosion prior to excavation or air pollutants and/or improper climatic conditions (temperature and relative humidity) inside the museum depositories. Considering the conclusions cited above, it follows that the study of the corrosion products phase composition is the most suitable to solve this problem.

Two methods, X-ray powder diffraction analysis (Lahanier, 1986) and infrared spectroscopy (Matteini et al., 1984), have been used for the study of the corrosion products observed on prehistoric and antique bronze artifacts from the collections of the National Museum in Prague. X-ray powder diffraction data of related minerals from the collections of the museum were used as a standard for comparison. Temperature and relative humidity in the depositories were controlled. Concentrations of important air pollutants in the area of the museum, its location in the city, and its elevation and wind directions were taken into consideration.

The complex analysis of all these available parameters will be described in this paper. X-ray powder diffraction analysis and infrared spectroscopy were the methods used for the solution of the problem.

## Methods

All patina samples (52 samples) were scraped from the twenty-four artifact surfaces using scalpel or other suitable dental tools after estimating the range of patina coating on the artifacts. It was difficult to remove the various patina layers as separate layers because of the manner in which the layers may intermix. A binocular microscope was used to observe the patina. As the individual patina phases were hardly distinguishable, it was not possible to separate the corrosion products. Table I lists the artifacts studied and the characteristics of their corrosion products.

For small samples, we used the Debye-Scherrer X-ray powder diffraction method (camera diameter 114.6 mm, Mikrometa Chirana, Cu K-alpha radiation, Ni filter, 35 kV, 20 mA, 20 hours). In the case of larger samples, the X-ray powder diffractometer Chirana was used (generator: Fe K-alpha radiation with Mn filter, 30 kV, 8 mA current tube; goniometer: scanning velocity  $2^{\circ} \cdot \text{min}^{-1}$ , chart velocity  $20 \text{ mm} \cdot \text{min}^{-1}$ ; ratemeter: counts/sec.  $3 \cdot 10^2$ , time constant 3 sec.). The data obtained were in good agreement with the X-ray powder diffraction data of the minerals expected in patinas from the mineralogical collections of the museum and with the X-ray standard powder diffraction data JCPDS (Berry, 1980). The infrared spectra of ten selected patina samples were measured at ambient temperature using a Nicolet MX 1E Fourier transform infrared spectrometer in the range of  $4000 - 400 \text{ cm}^{-1}$  in KBr discs. The preparation pressure of the disc was 6.62 MPa, dilution 1 : 1000.

## RESULTS AND DISCUSSION

The aim of our work was to study the corrosion products of pre-historic and antique bronze artifacts with regard to possible damage caused by  $\text{SO}_2$  and other air pollutants recently detected in the area of Prague.

We based our approach on the following facts and requirements:

1. The artifacts have been stored in the National Museum for several decades.
2. Prior to their excavation before World War II, the artifacts lay buried for centuries, exposed to the effects of the soil.
3. The artifacts were either not conserved or were minimally treated.
4. The artifacts were partly covered with green corrosion products. A part of their surface, however, remained covered only with an oxide layer.
5. Records have been kept of the temperature and the relative humidity in the depositories.
6. Natural and synthetic (polymer) varnishes, lacquers, and adhesives have not been applied in the depositories.
7. It was not possible to correlate the concentrations of pollutants outdoors and inside the museum depositories because the instruments were not sensitive enough to measure low levels inside the museum.
8. The artifacts and their corrosion products were documented using colour photography (not illustrated in this paper).
9. X-ray diffraction and infrared analyses were carried out on the samples of the corrosion products.
10. The results of the analyses of the corrosion products were correlated with the temperature and relative humidity in the museum depositories and the outdoor concentrations of the pollutants.

We would expect to find the following minerals in the patinas studied (Matteini et al., 1984 - modified):

### a) copper chlorides

atacamite	$\text{Cu}_2(\text{OH})_3\text{Cl}$
paratacamite	$\text{Cu}_2(\text{OH})_3\text{Cl}$
botallackite	$\text{Cu}_2(\text{OH})_3\text{Cl}$
nantokite	$\text{CuCl}$
eriochalcite	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

### b) sulphates

antlerite	$\text{Cu}_3(\text{OH})_4\text{SO}_4$
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brochantite	$\text{Cu}_4(\text{OH})_6\text{SO}_4$	
chalkanthite	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	
anglesite	$\text{PbSO}_4$	
gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	} both as deposits
anhydrite	$\text{CaSO}_4$	
c) <u>nitrates</u>		
gerdhardtite	$\text{Cu}_2(\text{OH})_3\text{NO}_3$	
d) <u>carbonates</u>		
malachite	$\text{Cu}_2(\text{OH})_2\text{CO}_3$	
azurite	$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$	
cerussite	$\text{PbCO}_3$	
calcite	$\text{CaCO}_3$	as deposit
e) <u>silicates</u>		
chrysocolla	$\text{Cu}_4\text{H}_4(\text{OH})_8(\text{Si}_4\text{O}_{10})$	
f) <u>phosphates</u>		
libethenite	$\text{Cu}_2(\text{OH})\text{PO}_4$	
g) <u>oxides</u>		
cuprite	$\text{Cu}_2\text{O}$	
tenorite	$\text{CuO}$	
cassiterite	$\text{SnO}_2$	
hydrocassiterite	$(\text{Sn}, \text{Fe})(\text{O}, \text{OH})_2$	
(varlamoffite)	$(\text{Sn})(\text{O}, \text{OH})_2$	

Approximately fifty compounds (oxides, sulphides, carbonates, chlorides, sulphates, etc.) found as corrosion products or deposits on copper and its alloys have previously been described (Riederer, 1985). Phase composition of the corrosion products studied is given in Table II. The climatic conditions prevailing in the area surrounding the museum are given in Table III.

As a result of the traffic increase of the last eight years, the values of  $\text{NO}_x$  and CO pollutants are higher while the value of  $\text{SO}_2$  pollution remains approximately at the same level. Coal combustion is probably the main source of  $\text{SO}_2$  pollution. Concentrations also vary significantly at different times of the year. The wind directions - predominantly northeastern (53 %), eastern (11.5 %), southwestern (12 %), and southern (10 %) - influence air pollution in the surroundings of the museum. The temperature and relative humidity in the depositories measured approximately 20 °C and less than 54 % respectively.

Fifty-two samples taken from twenty-four artifacts were analyzed. Table I lists their characteristics. The phase composition of the corrosion products studied and the deposits found on the surface of bronze artifacts is given in Table II. The distribution of mineral phases found in the samples studied yields the following information:

C u p r i t e,  $\text{CuO}_2$ , was found in 25 samples (~48 %); although it was present in all corrosion products, it was not separated in several cases. The presence of t e n o r i t e,  $\text{CuO}$ , was not proven. M a l a c h i t e,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ , was found in 36 samples (~70 %) and was the mineral most frequently observed in the corrosion products. A z u r i t e,  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ , was found in 1 sample only (~2 %). A t a c a m i t e,  $\text{Cu}_2(\text{OH})_3\text{Cl}$ , and its polymorph p a r a t a c a m i t e were observed in 13 (~25 %) and 5 (~10 %) samples respectively. N a n t o k i t e,  $\text{CuCl}$ , was not found. C e r u s s i t e,  $\text{PbCO}_3$ , was found in 5 samples (~10 %) and c a s s i t e r i t e,  $\text{SnO}_2$ , in 3 samples (~6 %). Special attention was paid to the possible presence of various copper hydroxosulphates of the b r o c h a n t i t e,  $\text{Cu}_4(\text{OH})_6\text{SO}_4$ , and a n t l e r i t e,  $\text{Cu}_3(\text{OH})_4\text{SO}_4$ , types. Such compounds are supposed to be formed upon the reaction of gaseous air pollutants as  $\text{SO}_2$ ,  $\text{SO}_3$  or  $\text{H}_2\text{SO}_4$  with copper oxides or carbonates covering the metal surface. B r o c h a n t i t e was identified as an admixture in the corrosion products of 4 samples taken from two artifacts. It represents only ~8 % of the whole number of samples studied. G e r d h a r d t i t e,  $\text{Cu}_2(\text{OH})_3\text{NO}_3$ , was not found.

The analytical results and further observations suggest that the corrosion products found on prehistoric and antique bronze artifacts from the collections of the National Museum in Prague had formed while they lay buried. No active corrosion was observed based on the approach described in CCI Note 9/1 "Recognizing Active Corrosion", 1986. There is no evidence to support the hypothesis that the cause of the corrosion products formation is due to the effects of air pollution inside the museum. While the concentrations of air pollutants in the area of the museum are relatively high, the location of the building is favourable, situated as it is away from the historical centre of Prague along the Vltava river at a higher elevation. The wind directions are also favourable; breezes blow almost every day. The ambient temperature in the museum depositories is approximately 20 °C; the relative humidity is in the range of 49 - 54 %.

#### Conclusions

1. The two methods - X-ray powder diffraction analysis and infrared spectroscopy - applied simultaneously proved to be effective and quick and thus the most suitable methods for the analysis of corrosion products on bronze artifacts.
2. Malachite was found as the main corrosion product. The others were atacamite, paratacamite, cerussite, cassiterite, and azurite. Some surface copper oxide corrosion was observed on all artifacts.
3. Copper hydroxosulphates of the brochantite type were found only as an admixture in the corrosion products of two bronze artifacts.
4. Air pollution (especially  $\text{SO}_2$  and  $\text{NO}_x$ ) in the area of the National Museum is significant. The location of the National Museum building in the city and the prevailing winds are, however, so favourable that, with regard to climatic and microclimatic conditions (temperature, relative humidity) in the museum depositories, no harmful effects of the air pollutants inside the museum can be expected.
5. On the basis of these observations, it follows that there has been no recent active corrosion on the artifacts.

#### References

- Buzek, F., Šrámek, J. "Sulfur isotopes on the study of stone monuments conservation." Studies in Conservation 30 (1985): 171-176.
- Berry, L. G., ed. Selected Powder Diffraction Data for Minerals. Joint Committee on Powder Diffraction Standards, Search Manual, Swarthmore: 2nd edition, 1980.
- Lahanier, Ch. "The powder diffraction pattern applied to the knowledge of works of art." Chemica Scripta 26A (1986): 47-55.



- Matteini, M.; Moko, A.; Lalli, C. "Infrared spectroscopy: a suitable tool for the characterization of components in bronze patinas." ICOM Committee for Conservation 7th Trienn. Meeting, Copenhagen 1984, Preprint 84/22/18-24.
- Recognizing Active Corrosion. CCI Note 9/1 Ottawa: 1986. Canadian Conservation Institute.
- Riederer, J. "Die Wirkung gasförmiger Schadstoffe auf Kunstgüter im inneren von Museen." Arbeitsblätter für Restauratoren H. 1, Gruppe 21 (1979): 17-20.
- Riederer, J. "Umweltschäden an Kunstwerken in Innenräumen." Jb. Preuss. Kulturbes. 18 (1981): 95-101.
- Riederer, J. "Analytische Methoden in der Kulturgeschichtlichen Forschung." Anal. - Taschenb. 5 (1985): 3-32.
- Sakař, V. "Roman imports in Bohemia." Fontes Archaeologici Pragenses Vol. 14 (1970): 72 pp., Museum Nationale Pragae.
- Směrnice hlavního hygienika ČSSR o nejvyšších přípustných koncentracích nejzávažnějších škodlivin v ovzduší. [Directions of the chief hygienist of the Czechoslovak Socialist Republic on the highest admissible concentrations of the most significant harmful substances in the atmosphere.] Ministerstvo zdravotnictví ČSR 1967. (Ministry of the Health of ČSR 1967.)
- Šrámek, J.; Buzek, F. "Isotopic composition of the sulfur incrustations on the chosen historical monuments in Prague." Sborník restaurátorských prací No. 1 1983 : 99-105. Státní restaurátorské ateliéry Praha. (State Restoration Studios Praha.)
- Veselý, J. "Emise a odumírání konifer." ["Emissions and Conifers dying away."] Vesmír 65 (1) (1986): 18-23.

Table I.: List and description of the artifacts studied and their corrosion products

artifact number	sample	the artifact inventory number	description of the artifact	patina characteristics
1		63,913/3	bowl fragment	fine, bright green
2		63,913/9	bowl fragment	fine, greyish green homogeneous
3	a	52,977	strainer	bright green
	b			bright green upper layer
				brown lower one
4	a	52,977	dipper	bright green upper layer
				brown lower one
	b			greenish brown
5	a	51,913	bucket	fine greyish green
	b			fine greyish green
6	a	52,979	bucket	bright green
	b			bright green
7	a	52,745	bucket	bright green upper layer
				brown lower one
	b			bright green upper layer
				brown lower one
8		53,265	caldron	greyish green upper layer
				deep brownish black lower one
9	a	55,710	flat bowl	bright green
	b			bright green
10	a	18,882	pot	green upper layer
				brown lower one
	b			brownish green
11	a	53,373	caldron	bright green upper layer
				brown lower one
	b			bright green upper layer
				brown lower one
	c			deep greenish black
	d			deep greenish black

Table I.: (continued)

arti- fact number	sam- ple	the arti- fact in- ventory number	description of the arti- fact	patina characteristics
12	a	54,297	caldron	bright green upper layer brown lower one
	b			bright green upper layer brown lower one
13	a	55,709/A	dipper	bright green upper layer brown lower one
	b			bright green upper layer brown lower one
	c			bright green upper layer brown lower one
	d			bright green
	e			bright green
	f			bright green upper layer brown lower one
14	a	51,856	bucket	fine greyish green
	b			fine greyish green
15	a	52,710	potsherd	greyish-whitish green
	b			greyish-whitish green
16	a	53,203	potsherd	whitish green upper layer brown lower one
	b			bright green
17	a	52,963	dipper	bright green
	b			bright green upper layer brown lower one
18	a	42,695	dipper fragment	bright green upper layer brown lower one
	b			fine greyish green
19		52,980	bowl	bright green upper layer brown lower one
20	a	52,978	dipper	bright green upper layer brown lower one
	b			greyish green upper layer redish brown lower one
	c			white layer
	d			greyish green
	e			whitish green
	f			white layer
21	a	52,780	bucket	bright greyish green
	b			bright greyish green
22		53,337	bucket	deep green upper layer brown lower one
23		1,238ant	Mercurial head	greyish green
24	a	1,501ant	pan	greyish green; white coating
	b			greyish green

The artifacts studied were excavated for the most part during the 1920s and 1930s.



Table II.: X-ray powder diffraction analysis of prehistoric and antique bronze corrosion products

artifact	sample	AT	PAT	M	C	BRO	CA	CE	AZ
1	*	+	+	-	-	-	-	-	-
2	*	+	+	-	-	-	+	-	-
3	a	+	-	-	-	-	-	-	-
	b	+	-	-	+	-	-	-	-
4	a	-	-	+	+	-	-	-	-
	b	-	-	-	+	-	-	-	-
5	a	-	-	+	-	-	-	-	-
	b	-	-	+	-	-	-	-	-
6	a*	-	-	+	-	-	-	-	-
	b	-	-	+	-	-	-	-	-
7	a*	+?	-	+	+	-	-	-	-
	b	+?	-	+	+	-	-	-	-
8	*	-	-	-	-	-	+	-	-
9	a	-	-	+	-	-	-	-	-
	b	-	-	+	-	-	-	-	-
10	a*	-	-	+	+	-	-	-	-
	b	-	-	+	+?	-	-	-	-
11	a	+	+	-	-	-	-	-	-
	b	+	+	+	-	-	-	-	-
	c	+	-	-	+	-	-	-	-
	d	+	-	-	+	-	-	-	-
12	a	-	-	+	+	-	-	-	-
	b	-	-	+	+	-	-	-	-
13	a	-	-	+	+	-	-	-	-
	b	+?	-	+	+	-	-	-	-
	c	-	-	+	+	-	-	-	-
	d	-	-	+	+?	-	-	-	-
	e	-	-	+	-	-	-	-	-
	f	+	-	+	+	-	-	-	-
14	a	-	-	+	-	-	-	-	-
	b	-	-	+	-	-	-	-	-
15	a	-	-	+	-	-	-	-	-
	b	-	-	+	-	-	-	-	-
16	a	-	-	+	+	-	+	-	-
	b	-	-	+	+?	-	-	-	-
17	a*	-	-	+	-	+	-	-	-
	b	-	-	+	+	+	-	-	-
18	a	-	+	+	+	-	-	-	-
	b	-	-	+	-	-	-	-	+
19		+	-	+?	+	-	-	-	-
20	a	+	-	-	+	-	-	-	-
	b	-	-	+	-	-	-	+?	-
	c	-	-	+?	-	-	-	-	-
	d	-	-	+	-	-	-	-	-
	e	-	-	-	+?	-	-	+	-
	f	-	-	-	-	-	-	+	-
21	a	-	-	+	-	-	-	-	-
	b	-	-	+	-	-	-	-	-
22	*	+	-	-	+	-	-	-	-
23	*	-	-	-	-	-	-	+	-
24	a	-	-	+	-	+	-	-	-
	b	-	-	+	-	+	-	-	-

AT = atacamite, PAT = paratacamite, M = malachite, C = cuprite, BRO = brochantite, CA = cassiterite, CE = cerussite, AZ = azurite

+ = present, - = absent, ? = uncertain

Phase composition of all samples was determined using the X-ray powder diffraction analysis and verified by the infrared spectroscopy (in the cases signed with an asterisk).

Table III.: The climatic conditions in the area surrounding the National Museum in Prague

	ref.10		1978*		1983		ref.1	
	a)	b)	Oct.	Nov.	May	Nov.	c)	d)
SO <sub>2</sub>	500	150	220	220	21	185	180	30
NO <sub>x</sub>	500	150	100	170	373	145	200	40
CO	6000	1000	1530	3130	4573	4450	5000	1000
dust	500	150	167		215			
tempe- rature °C			10.9	6.7	15.5	3.6		
relative humidity %			88	76	71	85		
traffic cars/hour			355	662	1278** 1700***			

Concentrations of pollutants are given in  $\mu\text{g}\cdot\text{m}^{-3}$

- a) the highest admissible short-term concentration
- b) the highest admissible average day concentration
- c) the measurement at the Vltava valley during winter
- d) the measurement at the higher area of Prague during summer
- \* the measurements were carried out for comparison of the values before and after opening the north-south motorway
- \*\* the average value during 24 hours
- \*\*\* the average value during waking hours

The average yearly SO<sub>2</sub> concentration in the central Prague atmosphere exceeds  $150 \mu\text{g}\cdot\text{m}^{-3}$  (Vesely, 1986)



**ANALYSES DE PIGMENTS BLANCS APPLIQUEES A L'ETUDE CHRONOLOGIQUE  
DES PEINTURES DE CHEVALET - BLANC DE TITANE**

C Couptry, J Le Marec, J Corset  
LASIR  
2 rue Henri Dunant, BP 28,  
94320 Thiais

M C Papillon, R Lefèvre  
Laboratoire de Microscopie  
Analytique Appliquée,  
Université de Paris XII  
94019 Creteil

A Duval, Ch Lahanier, JP Rioux  
Laboratoire de Recherche des  
Musées de France  
Palais du Louvre  
75041 Paris

L'authenticité des tableaux modernes est un problème d'une grande importance qui se pose en particulier à l'occasion d'acquisitions. Faute de moyens précis de datation, les laboratoires doivent actuellement développer de nouvelles méthodes d'analyse dont les résultats comparés à des critères chronologiques établis avec certitude permettront de mettre en évidence d'éventuels anachronismes.

Préparé industriellement depuis 1917, le blanc de titane présente à cet égard un intérêt particulier. Ses qualités pigmentaires, comme son bon pouvoir opacifiant, lié à son indice de réfraction élevé, sa relative stabilité chimique et sa non toxicité ont rapidement stimulé son usage en peinture et le développement de sa production. L'intérêt pour ce pigment s'est aussi manifesté par de nombreuses recherches visant à améliorer les procédés de fabrication. L'étude de cette évolution, talonnée de brevets, permet de dégager des dates charnières qui peuvent servir de critères chronologiques.

L'objet de cette étude est de présenter des techniques d'analyses adaptées à la taille limitée de prélèvements issus de tableaux modernes et permettant de mesurer précisément différents paramètres physiques du pigment afin de disposer de résultats caractéristiques de ses diverses variétés.

#### I Evolution des modes de fabrication du blanc de titane

Le blanc de titane est un pigment blanc contenant de l'oxyde de titane,  $TiO_2$  sous deux formes cristallines différentes, l'anatase et le rutile, toutes deux de structure quadratique avec 4 motifs par maille pour l'anatase et 2 pour le rutile.

Plusieurs modifications des procédés industriels de fabrication permettent de préciser chronologiquement la nature du blanc de titane utilisé.

Les premiers pigments blancs au titane sont en fait des produits composites. Un  $TiO_2$  à structure d'anatase (25%) coprécipité avec  $BaSO_4$  ou  $CaSO_4$  (75%) est préparé par Barton et Rossi dès 1914. Des recherches menées parallèlement en Norvège par Farup conduisent à la première production industrielle en 1918 d'une anatase dont la concentration en  $TiO_2$  varie de 19% à 65% selon la qualité, les autres constituants étant  $ZnO$  ou  $BaSO_4$ .

En 1923 - 1924 les premiers blancs de titane purs (concentration en  $TiO_2$  supérieure à 95%) apparaissent en France : il s'agit d'anatase fabriquée par attaque sulfurique à chaud du minéral de titane : l'ilménite.

La commercialisation du blanc de titane par les fabricants de couleurs fines pour artistes ne commence qu'un peu plus tard en France : 1925 (Société Bourgeois) et 1927 (Société Lefranc).

En 1941 les premiers blancs de titane à structure rutile apparaissent sur le marché américain. Ils ne sont exportés puis produits en Europe qu'après la fin de la Seconde Guerre mondiale.

En 1949 Dupont de Nemours introduit un nouveau rutile pur préparé par un nouveau procédé dit "au chlore" où le minéral est chloré en milieu réducteur.

Afin d'améliorer les qualités pigmentaires du rutile (diminution du farinage et augmentation de la mouillabilité) des rutilés traités sont fabriqués dès 1950 aux USA : les particules submicroniques de  $\text{TiO}_2$  sont enrobées par une pellicule extrêmement mince (quelques nanomètres) d' $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  ou, plus tard, de  $\text{ZrO}_2$ . Ce type de pigment n'est produit en Europe qu'à partir de 1956.

La production des anatases composites s'arrête en Europe en 1971. Une production transitoire d'anatase pure par le procédé "au chlore" a eu lieu aux USA de 1975 à 1985.

De cette évolution se dégagent six dates (1) qui peuvent servir de critères de datation de peintures contenant du blanc de titane.

- Absence de blanc de titane avant 1918
- Anatases composites à partir de 1918
- Anatase pure à partir de 1922
- Rutile pur (procédé au sulfate) à partir de 1941 aux USA et de 1946 en Europe
- Rutile pur (procédé au chlore) à partir de 1949
- Rutilés traités à partir de 1950 aux USA et de 1956 en Europe
- Anatase (procédé au chlore) à partir de 1975.

## II Mise au point d'une méthodologie pour la caractérisation du blanc de titane

Cette étude nous a amené à tester les possibilités de différentes techniques d'analyse de microéchantillons. Dans les cas où la présence de titane a été observée, nous avons alors précisé la nature et la structure cristalline du composé dans lequel cet élément était engagé. L'espèce chimique recherchée dans cette étude étant essentiellement l'oxyde de titane  $\text{TiO}_2$ , nous avons effectué un certain nombre d'analyses préliminaires sur des échantillons de produits industriels : pigments purs en poudre, enrobés ou non<sup>1</sup>, puis mélangés à un liant, avec ajout de siccatifs<sup>2</sup>.

### II - 1 Identification du titane et d'éléments du pigment.

Par microfluorescence X (MFX)(2), on peut aisément identifier le titane et certains autres éléments présents dans le pigment, ajouts ou impuretés. L'analyse de divers blancs de titane en poudre de fabrication récente ainsi que des mélanges avec un liant, spécialement préparés par Lefranc-Bourgeois (Le Mans, France) (Tableau 1) montre que les pigments non enrobés sont quasi-purs (traces de Cu systématiquement décelées).

L'analyse par MFX a une sensibilité suffisante pour identifier le zirconium alors que par microanalyse électronique par sélection des énergies des rayons X on déce le l'aluminium et le silicium, éléments constitutifs de l'enrobage (tableau 1). Les teneurs obtenues par microanalyse électronique en sélection d'énergie sont voisines de celles du contrôle industriel. Les concentrations (quelques pour cent) mesurées sur des agglomérats de grains voisins de  $0.5\mu\text{m}$ , correspondent à des couches d'enrobage de quelques nanomètres.

La détection de l'un des 3 éléments à l'état de trace sur une couche contenant du titane ne peut cependant n'être qu'un indice de la présence de rutile traité car il peut aussi être lié à l'ajout de siccatifs par les fabricants de couleur ou à un mélange de couleurs réalisé par l'artiste.

### II - 2 Identification de la structure cristalline

La diffraction X est un moyen classique d'analyse cristallographique d'un échantillon isolé, même de petites dimensions (chambre de Gandolfi). Quand un microéchantillon se présente sous forme de coupes transversales, seul le microdiffractomètre X Rigaku permettrait d'opérer ponctuellement, la limite inférieure de la plage analysée étant de l'ordre de  $30\mu\text{m}$ , généralement supérieure à l'épaisseur d'une couche picturale.

1 - Nous remercions les sociétés Bayer, Tioxide, Thann et Mulhouse, Laporte pour la fourniture gracieuses d'échantillons.  
2 - Les échantillons ont été préparés par Monsieur RICCARAND, chef du laboratoire de la Société Lefranc Bourgeois que nous remercions.



Source	Types	Structure	% TiO <sub>2</sub> (1)	Traitement d'enrobage (1)	M.F.X. (Z > 18) traces	MEB (Z > 10)			
						Al	Si	Zn	K
BAYER	A	Anatase	99	--	- - Cu -	--	--	--	--
	RK-B2	Rutile traité	94	Al, Si, org.	- - - -	1,2±0,5	--	--	--
	RK-B4	Rutile traité	94	Al, Si, Zr, org.	- - Cu Zr	2,3±0,5	--	--	--
Kronos	A	Anatase	99	--	- - - -	--	--	--	0,3
	RKL	Rutile	99	--	Zn - Cu -	--	--	--	--
	RN59	Rutile traité	95	Al, Si	- - - -	2,6	--	--	--
	CL310	Rutile traité	93	Al, Si, Zr,	- - Cu Zr	4 ± 0,5	--	--	--
TIOXIDE	A-HR	Anatase	98,7	--	Ni Fe Cu -	--	--	--	0,3
	RTC90	Rutile traité	94	Al, org	- - Cu -	3,6±0,5	--	--	--
	R-CR2	Rutile traité	93	Al, Si, org.	Zn Fe - -	2,1 1,4±1	--	--	--
	R-SM3	Rutile	99	org.	- - Cu -	--	--	--	0,3
THANN et MULHOUSE	AT1	Anatase	99	--	- - Cu -	--	--	--	0,3
	REX	Rutile	99	--	- - Cu -	2	--	--	--
	RL68	Rutile traité	94	Al, Si	Zn - - -	2,1±0,5	--	--	--
LAPORTE (SCM)	Trona 388	Rutile traité	--	--	- - - -	4	5,5	--	--
	Roma 552	Rutile traité	--	--	Zn - - -	2	--	--	--
	LFB4	Rutile traité	--	--	- - - -	--	--	--	--
LEFRANC- BOURGEOIS	Rutile	KRONOS RKL	--	--	- - Cu -	--	--	--	--
	Rutile	KRONOS RN59 traité	--	--	- Fe Cu -	2,7	--	--	--
	RKL	+ huile	--	--	- Fe Cu -	--	--	--	--
	RKL	+ huile + siccatifs	--	--	- - - Zr	--	--	--	--
	RKL	+ huile + ZnO	--	--	Zn - - -	--	--	--	--
	RKL	+ huile + ZnO + siccatifs	--	--	Zn Co Ca Zr	--	--	--	--

(1) information donnée par le fabricant

(2) Spectrométrie X à sélection d'énergie - concentration exprimée en % pondéral d'oxyde.

TABLEAU 1 : Analyses d'échantillons de TiO<sub>2</sub> (poudre ou mélange avec un liant)

### Spectrométrie de diffusion Raman

La microspectrométrie Raman présente plusieurs avantages : elle peut identifier anatase et rutile avec une résolution spatiale de l'ordre du micromètre (3). L'analyse peut donc être effectuée sur microprélèvement ou, sans préparation supplémentaire, sur chaque couche d'une coupe stratigraphique de matière picturale.

La spectrométrie de diffusion Raman caractérise un composé par ses états vibrationnels liés à la nature des liaisons chimiques et à la structure de l'édifice polyatomique formant le composé. Malgré l'étroite parenté de l'anatase et du rutile (les seuls paramètres qui les différencient sont ceux de leur maille cristalline), on doit obtenir des spectres Raman différents liés à la différence de leur réseau cristallin. Les échantillons étudiés par cette technique, non destructive ne demandent aucune préparation d'où une mise en oeuvre très aisée. Mais le signal de diffusion Raman peut être masqué par la fluorescence du composé, ses impuretés ou des adjonctions faites. Une série d'échantillons en poudre de rutile et d'anatase de fabrications différentes a été examinée afin de voir d'éventuelles variations dans les fréquences des raies obtenues, qui concordent avec les données de la littérature(4), ce qui permet d'identifier aisément l'un ou l'autre des composés: l'anatase présente une raie très intense à 144 cm<sup>-1</sup>, accompagnée de raies plus faibles à 197, 393, 515, 635 et 796 cm<sup>-1</sup> alors que les raies du rutile ont des intensités voisines à 448 et 612-1 et des intensités plus faibles à 141, 235, 826 cm<sup>-1</sup>.

L'oxyde de zinc et le sulfate de baryum peuvent être associés au blanc de titane: ZnO sera difficilement identifiable par spectroscopie Raman en présence de rutile, bande à 436 cm<sup>-1</sup> pour l'un et à 448 cm<sup>-1</sup> pour l'autre, tandis que le sulfate de baryum présente une bande isolée à 980 cm<sup>-1</sup> permettant de le caractériser. L'étude de mélanges rutile/anatase dont la concentration en rutile varie de 98 à 50% montre la possibilité d'une évaluation grossière du pourcentage d'anatase, par le rapport des hauteurs de certains pics, technique déjà développée sur des échantillons non microscopiques(5).

Enfin des échantillons test préparés par Lefranc-Bougeois, à partir de TiO<sub>2</sub>, ZnO, d'huile et différents siccatifs, ne montrent pas de fluorescences importantes gênant l'obtention du spectre Raman.

Lorsque la fluorescence de certains liants masque le signal de diffusion Raman, l'identification de la structure cristalline du blanc de titane, bien que difficile à obtenir, peut cependant être effectuée en META.

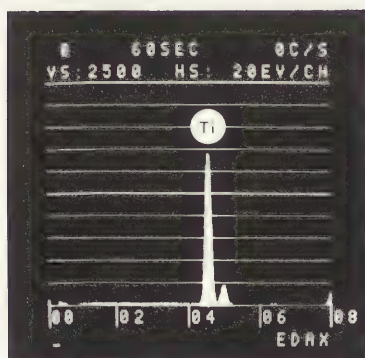


Fig. 4 - Microanalyse électronique du rutile et de l'anatase purs.

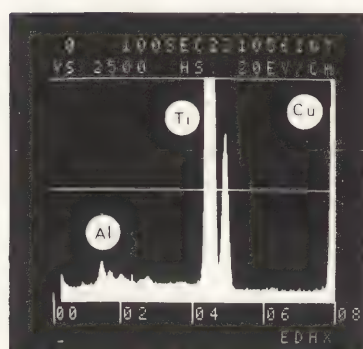


Fig. 5a - Microanalyse électronique du rutile traité AKB4 (la raie du Cu est due à la grille supportant la coupe ultrafine).

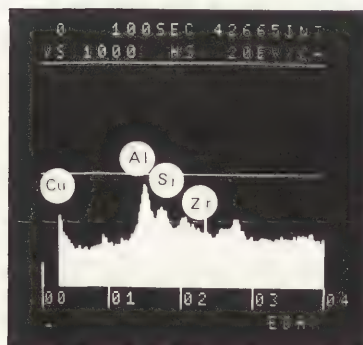


Fig. 5b - Microanalyse électronique du rutile traité AKB4 - Dilatation de la partie gauche du spectrogramme de la fig. 5a.

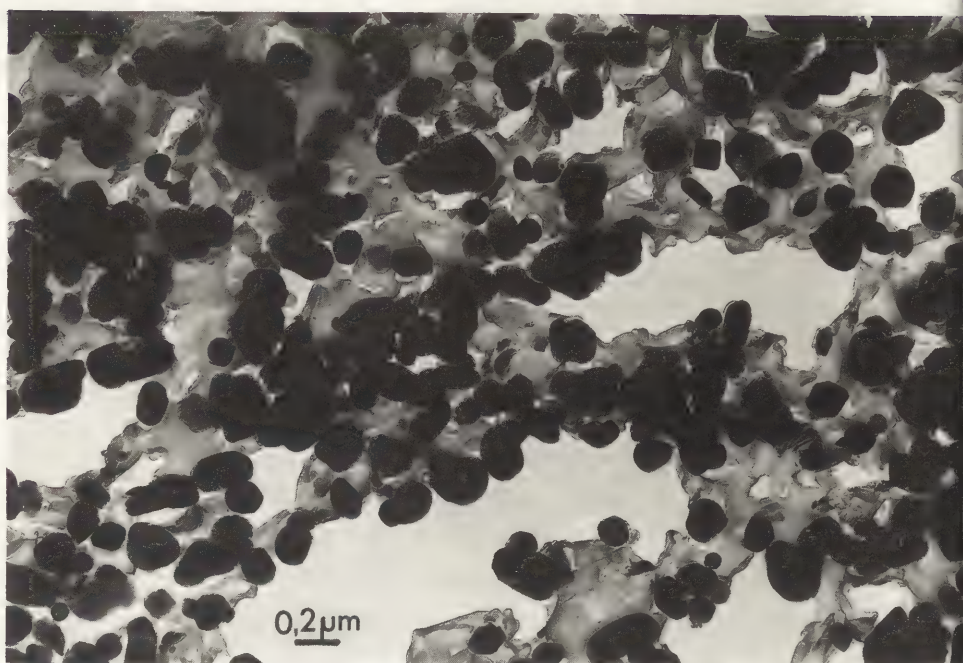


Fig. 1 - Microscopie Electronique en Transmission de grains de rutile pur.

#### Microscopie électronique en transmission analytique (META)

Des poudres-témoins de trois types d'oxyde de titane ont été étudiées :

- anatase pure
- rutile pur (R K L)
- rutile traité par Al, Si, Zr et matériaux organiques (AKB4)

Leur préparation en vue de la META s'est faite selon le protocole décrit par ailleurs dans ce même volume (6). Les coupes ultrafines obtenues ont une épaisseur inférieure à 100 nm (1000A).

Les figures 1, 2 et 3 illustrent la morphologie de grains de rutile pur, anatase pure et rutile traité AKB4 à des grossissements voisins<sup>3</sup>. On remarquera quelques artefacts de préparation (déchirures dans la résine d'inclusion) et l'hétérogénéité granulométrique de l'anatase. La fine pellicule de traitement du rutile AKB4 n'est pas apparue, même à de très forts grossissements (épaisseur estimée à 5 à 8 nm).

La microanalyse Electronique par Sélection des Energies des Rayons X émis sous le faisceau du Microscopie Electronique à Transmission<sup>3</sup> ne révèle la présence que du Ti dans le rutile ou l'anatase pure (fig. 4). Par contre, la fine pellicule de traitement du rutile AKB4, est responsable de l'apparition des raies de Al, Si et Zr sur des spectres réalisés simultanément sur plusieurs grains de ce rutile traité afin d'augmenter les volumes émissifs (la raie de Cu est due à la grille sur laquelle sont déposées les coupes ultrafines) (fig. 5a et b).

3 - Etudes réalisées sur un Microscopie Electronique à Transmission JEOL 100C équipé d'un Sélecteur des Energies des Rayons X EDAX 711 - (Laboratoire d'Etude des Particules Inhalées, DASES, F-75013 PARIS - A GAUDICHET, M A BILLON-GALLAND et G PETIT, réalisatrices.



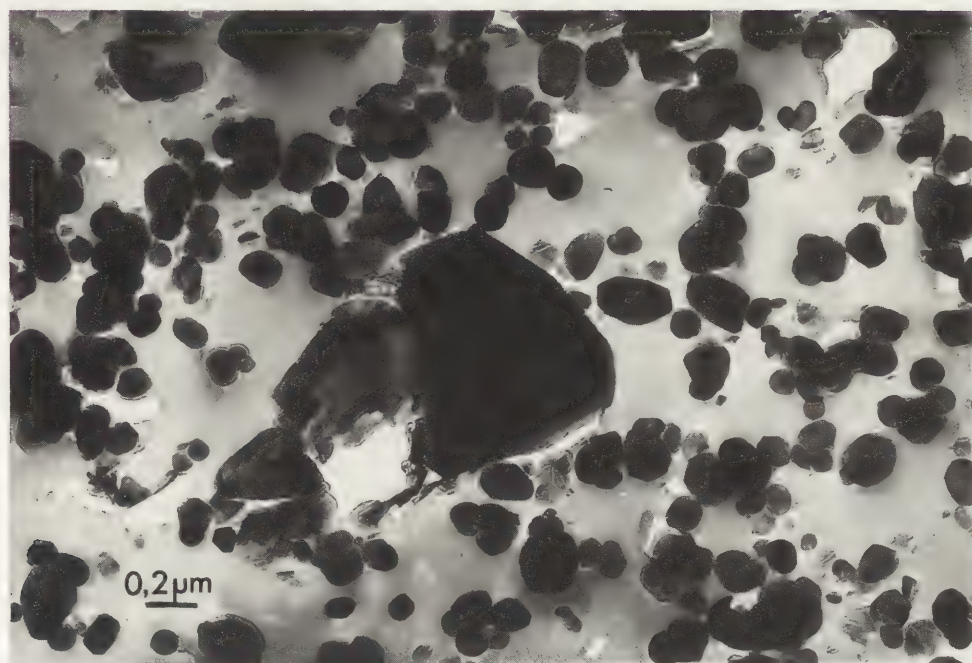


Fig. 2 - Microscope Electronique en Transmission de grains d'anatase pure.

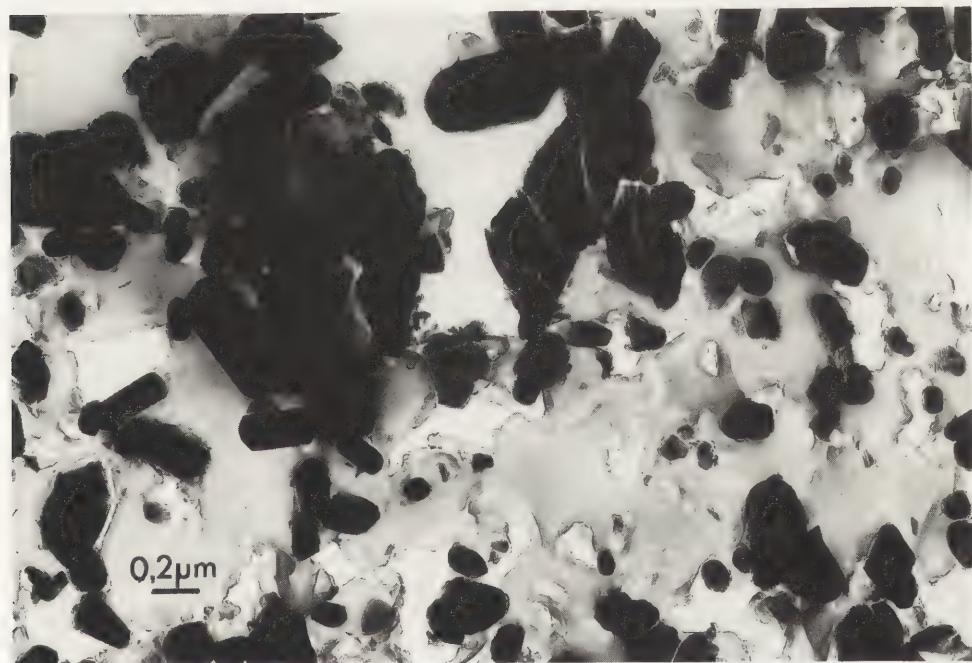


Fig. 3 - Microscope Electronique en Transmission de grains de rutile traité AKB4.

Afin de confirmer les résultats de la microanalyse des grains de rutile traité AKB4 nous avons recommencé leur Microanalyse par sonde Electronique en Transmission en réalisant une Spectrométrie des longueurs d'onde des Rayons X émis sous le faisceau électronique<sup>4</sup>. Les raies de Ti, Al, Si et Zr sont présentes sans ambiguïté.

Une caractérisation a été faite par Microdiffraction Electronique<sup>5</sup> sur deux grains, l'un de rutile (fig. 6), l'autre d'anatase (fig. 7). Les paramètres des mailles cristallines, calculés à partir des clichés obtenus, sont effectivement ceux des deux formes de l'oxyde de titane.



Fig. 6 - Diagramme de microdiffraction des électrons par le rutile pur.

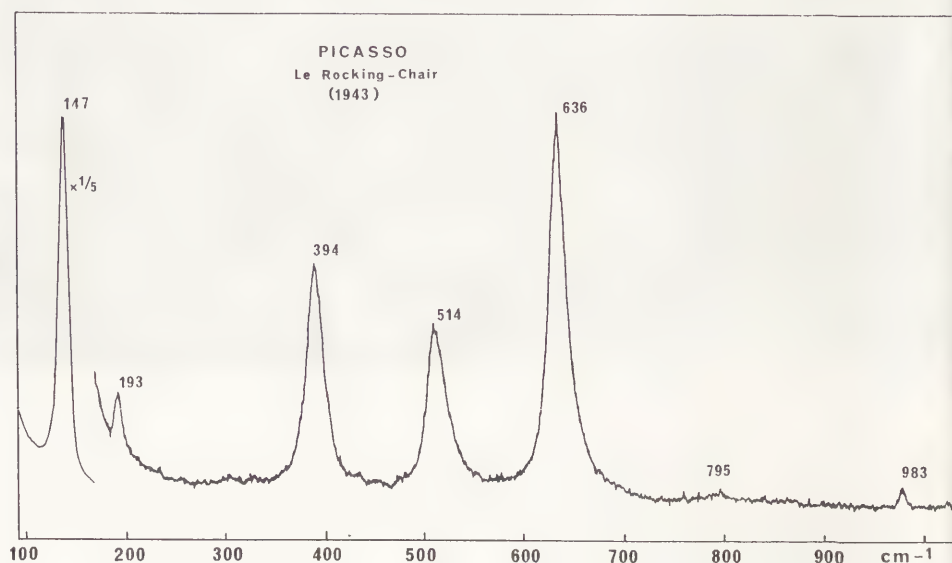


Fig. 8 - Spectre Raman d'un microéchantillon de couleur blanche caractérisant l'anatase. Présence probable de sulfate de baryum.



Fig. 7 - Diagramme de microdiffraction des électrons par l'anatase pure.

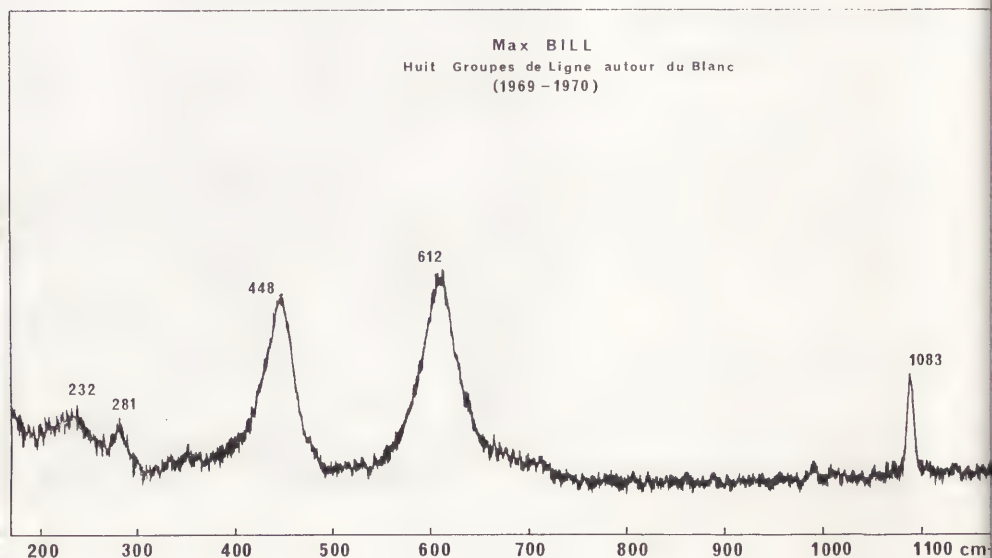


Fig. 9 - Spectre Raman d'un microéchantillon de couleur blanche caractérisant le rutile.

4 - Service Commun de Microanalyse de l'Université Paris XII (Faculté de Médecine, F.94010 CRETEIL, Microsonde Electronique en Transmission CAMEBAX (P. BOUMATI, réalisateur).

5 - Laboratoire de Minéralogie-Cristallographie de l'Université Paris VI. Microscope Electronique à Transmission JEOL 100 C, équipé d'une platine goniométrique eucentrique (M GANDAIS, réalisation).



### III Validation de la caractérisation du blanc de titane en peinture moderne et contemporaine

La microfluorescence X permet d'identifier directement sur un tableau la présence de titane localisant ainsi l'emplacement du prélèvement à opérer. La microspectrométrie Raman permet ensuite de caractériser la forme cristalline du pigment. Nous pouvons ainsi déterminer si les résultats obtenus sur des tableaux datés sont cohérents avec la chronologie de la fabrication du titane.

Trente sept tableaux du Musée National d'Art moderne datés de 1920 à 1980 ont été étudiés. La présence de titane n'apparaît que dans onze cas, tous postérieurs à 1943. Les prélèvements effectués<sup>6</sup> sur les tableaux contenant du titane donnent les résultats résumés sur le tableau 2. Deux exemples de spectres Raman sont présentés (fig. 8 et 9).

Ils suggèrent les commentaires suivants :

- identification sans équivoque en spectrométrie Raman de l'anatase (spectre 1) ou du rutile (spectre 2)
- décalage d'une vingtaine d'années entre l'apparition du blanc de titane dans le commerce général et son utilisation effective par les artistes, ce pour les quelques tableaux étudiés.
- la présence de zinc est décelée par MFX dans la plupart des échantillons alors qu'aucun composé de zinc n'est identifié par spectrométrie Raman.
- dans les 2 tableaux de Picasso, présence de raies Raman supplémentaires ( $983\text{ cm}^{-1}$ ) attribuables vraisemblablement au sulfate de baryum (présence de baryum révélée par MFX.) Les spectres Raman obtenus à partir des tableaux de Gorky ou de Penck, ne montrent aucune raie supplémentaire malgré la présence de baryum dans le spectre MFX.

LISTE DES TABLEAUX ECHANTILLONNES CONTENANT DU TITANE  
(MNAM)

Date	Peintre	Tableau	MFX	Raman <sup>a</sup>
1943	Picasso	Le rocking-chair	Ti, Zn, Pb, Sr, Ba	anatase + $\text{SO}_4\text{Ba}$
1945	Ashile Gorky	Table-paysage	Ti, Ba, Zn, Sr	anatase
1951	Serge Poliakoff	Composition gris et noir	Ti, Ca, Sr, Zn, Ba, Pb	anatase
1953	Jackson Pollock	The deep	Ti	anatase
1956	Picasso	Deux femmes sur la plage devant la mer	Ti, Zn, Sr, Ba	anatase + $\text{SO}_4\text{Ba}$
1962	Barnett Newman	Not there, here	Ti, Ba (traces), Zn	rutile
1963	Niki de St Phalle	La mariée	Ti, Ca, Zn	rutile
1968-70	Dubuffet	Le jardin d'hiver	Ti, Zn	rutile
1969-70	Max Bill	Huit groupes de lignes autour du blanc	Ti, Zn, Pb	rutile
1974	Miró	Personnages, oiseaux dans la nuit	Ti, Zn, Ba (traces)Pb, Sr	anatase
1976	Penck	TM 1976	Ti, Zn, Ba, Sr	rutile

<sup>a</sup> Les spectres Raman ont été obtenus avec la microsonde Raman MOLE de JOBIN-YVON (Laboratoire de spectrochimie Infra-rouge et Raman -CNRS - Thiais); conditions expérimentales:  $\lambda = 488\text{ nm}$ , puissance laser 60 mW, fente spectrale  $8\text{ cm}^{-1}$  objectif 1000x)

Tableau 2

6 - Nous remercions Monsieur Bernard CEYSSON, Directeur du Musée National d'Art Moderne, Centre Georges Pompidou, Paris, de nous avoir autorisé à opérer des prélèvements sur les tableaux des collections du Musée et Monsieur Jacques HOURRIERE, Chef du Service de Restauration, pour l'aide précieuse qu'il nous a procurée.

### CONCLUSION

Par microfluorescence X on peut déceler la présence de titane sur un tableau sans prélever de matière picturale. Sur un prélèvement judicieusement choisi grâce à cette analyse (dimension qui peut être limitée à un échantillon de quelques micromètres), la spectrométrie Raman caractérise la nature cristalline de l'oxyde de titane. En cas de fluorescence due au liant, l'analyse structurale peut être effectuée par microscopie électronique en transmission analytique. L'étude de caractérisation de l'enrobage pourra être poursuivie à l'aide de cette dernière technique.

Ces moyens analytiques permettent d'établir la chronologie effective de l'utilisation du blanc de titane de peinture fine pour artistes et de la comparer à celle de sa fabrication. Ces nouveaux critères serviront à résoudre des problèmes d'authenticité.

### BIBLIOGRAPHIE

1. Bego P. et Vercier P., Monographie de Muséologie, (4ème année de l'Ecole du Louvre), "Étude scientifique d'une Ecole ou d'un peintre primitif, classique ou moderne. Préciser l'apport des méthodes optiques, physico-chimiques, informatique de Laboratoire à la connaissance des oeuvres. Limites actuelles, possibilités de cette approche : blanc de plomb, blanc de titane, 1986
2. Lahanier Ch., "Application des techniques de fluorescence X. International Symposium on the Conservation and Restoration of Cultural Property, Tokyo, 1979.
3. Delhay M. et DHAMELIN COURT P., "Raman microprobe and microscope with laser excitation", Journal of Spectroscopy, tome 3, p.33.
4. Griffith W.P., "Raman spectroscopy of terrestrial materials in : Infra-red and Raman spectroscopy of lunar and terrestrial materials", Karr C. ed., Academic Press, New York, 1975.
5. Capwell R.J., Spagnolo S. et Desea M.A., "A rapid determination of low concentration of anatase in rutile TiO<sub>2</sub> pigments by Raman spectroscopy, Applied Spectroscopy, Vol 26, n°5, pp 537-539.
6. Papillon M.C., Lefèvre R., Lahanier Ch., Duval A., Rioux J.P. "Réalisation et étude par microscopie électronique analytique en transmission de coupes ultra-fines d'échantillons de peintures", ICOM CC 8th Triennial Meeting Preprints, September 1987.



## SUMMARY

Microchemical tests are described for some important modern pigments used by artists. The tests using concentrated sulphuric acid, concentrated nitric acid and concentrated alcoholic potassium hydroxide were applied to paint cross-sections to identify the pigments used. These microchemical tests enabled correct identification of the modern organic artists' pigments.

## MICROCHEMICAL IDENTIFICATION OF MODERN ORGANIC PIGMENTS IN CROSS-SECTIONS OF ARTISTS' PAINTINGS

M. de Keijzer

Central Research Laboratory for Objects of Art and Science  
Gabriël Metsustraat 8  
1071 EA Amsterdam, The Netherlands

## Introduction

Whereas the use of natural pigments dates back to antiquity, the synthetic organic pigments so widely known today were not used until the second half of the nineteenth century. Seven years after the synthesis of mauve by Sir William Perkin in 1856, a lake of the dye was used to print the 1863 British six-penny stamp. Between 1856 and 1915 the lake colours and azo-pigments were discovered (Figure 1 and 2). From 1915 to about 1930 the pigments developed earlier were applied on a large scale. From 1930 there began a search for better pigments, particularly those having improved lightfastness (1). Most organics developed during the nineteenth century were insufficiently permanent for the purpose of art. Seduced by the brilliance of the new colours, however, many artists used them with disastrous results; hence the terms "coal-tar" and/or "aniline" colours for synthetic organics were the opposite of flattering. An exception, however, was madder lake (1,2-dihydroxyanthraquinone), the first natural dyestuff to be produced in a pure form in 1868. The twentieth century saw the appearance on the artists' palettes of some organic pigments, which were more stable and lightfast than many inorganics.

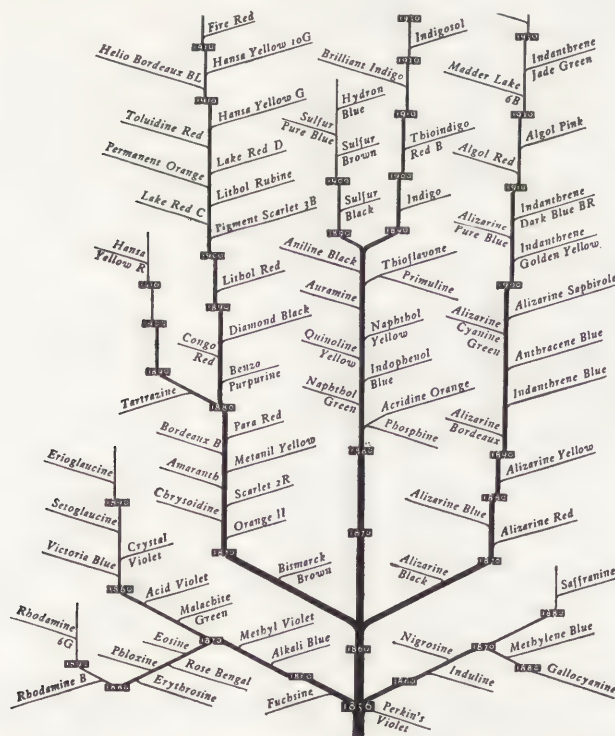


Fig. 1. Significant Developments in Organic Color Chemistry. (Courtesy of Interchemical Corporation.)

The many developments of this modern period include the use of such artists' pigments as: copper phthalocyanine blue PB 15, halogenated phthalocyanine PG 7 and PG 36 (phthalocyanine green), linear-trans-quinacridone PV 19, carbazole dioxazine violet PV 23 and Hansa yellow G PY 1. The invention and start of industrial production of these pigments can be ascertained by patents. Prejudice against "coal-tar" colours gradually subsided and is no longer of any real consequence (2).

When the artists started to use these modern organic pigments is little known. Because of the sometimes disastrous results achieved with many organic pigments artists kept using for their conventional pigments of which the quality was assured.

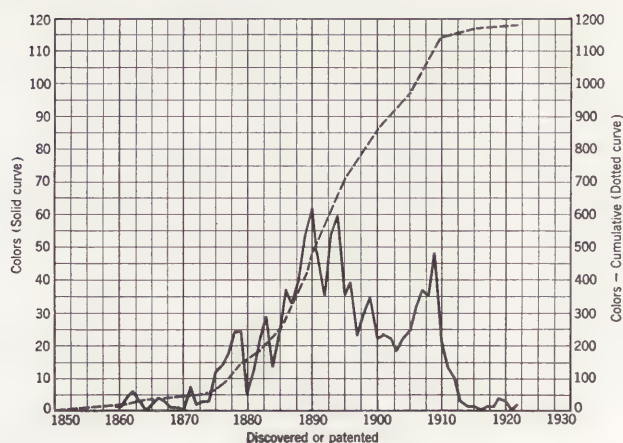


FIG. 2. Dyestuffs.

Table 1

Survey of the modern artists' palette

colour	pigment
white	white lead, zinc oxide (zinc white), lithopone, titaniumdioxide (rutile-modification and anatase-modification)
black	bone black, lampblack
blue	synthetic ultramarine blue, cobalt blue, cerulean blue, manganese blue, Prussian blue, phthalocyanine blue
green	green earth, chromium oxide (hydrated and anhydrous)
yellow	halogenated phthalocyanine (phthalocyanine green)
orange	yellow ochre, cadmium yellow, chromate yellows, Hansa-yellows
red	cadmium orange, Hansa-orange
violet	cadmium red, madder lake, red ochre, linear-trans-quinacridone
brown	carbazole dioxazine violet, cobalt violet, manganese violet, linear-trans-quinacridone, ultramarine violet
	brown ochre, brown umber

In general, many pigments of the nineteenth century and earlier are still used today. Inorganic and organic pigments used in the twentieth century include: titanium dioxide (anatase-modification), titanium dioxide (rutile-modification), cadmium red, phthalocyanine blue, halogenated phthalocyanine, linear-trans-quinacridone, carbazole dioxazine violet and the Hansa-yellows. These recent pigments make it possible to provide more accurately a date "post quem" for art-objects.

Microchemical identification of modern organic artists' pigments in paint cross-sections by colour-reactions

Among the many qualitative tests which can be applied for the identification of organic colouring matters, the oldest, simplest and most specific is the test based on reactions with concentrated sulphuric acid. The characteristic colour-changes produced by the concentrated sulphuric acid generally serve as an excellent means of identification. The action of this reagent upon dyes and pigments is almost instantaneous.

Along with concentrated sulphuric acid, concentrated nitric acid and concentrated alcoholic potassium hydroxide are used to produce different colour reactions.

These reactions can reliably identify pigments, because no two organic pigments, having crystals with different chemical structures, produce the same colour reactions. These chemical tests offer the advantage of being applied to small paint-samples without the need for separation of layers. The relatively quick method, which is effective in colour discrimination is also cheap and easy to apply.

Its major disadvantages are its destructiveness and the fact that it is not suitable for every colour (3).



Procedure

A small drop of one of the reagents is applied to the polished surface of the paint cross-section and covered with a microscope glass cover slip to protect the instrument and remove air-bubbles. A magnification of 200 to 400 times is used to observe the change of colour for approximately three minutes, after which the coloured surface is polished with silicon carbide paper of 4000 mesh. Another reagent is then added to the fresh paint-surface and again covered with a microscope glass cover slip.

Table 2

Reactions of some important modern organic artists' pigments in paint cross-sections

Pigments	Reagents and reactions		
	concentrated sulphuric acid	concentrated nitric acid	concentrated alcoholic potassium hydroxide
Copper phthalocyanine, PB 15 date of appearance 1928 date of production 1935	solid turns green/yellow, time = 0' then dissolves to a colourless solution, time = 3' to 15'	solid turns purple, time = 0' or green then purple, time = 3' to 15'	no change
Halogenated phthalocyanine (phthalocyanine green), PG 7 and PG 36  date of appearance 1935 date of production 1936	solid turns yellow, time = 0' to 3' and dissolves	no change	no change
Linear-trans-quinacridone, PV 19 date of appearance 1935 date of production 1958	dissolves to give mauve, then colourless solution, time = 3'	solid becomes purple, time = 0'	blue dye emitted from edges time = 0', then flake blue, time = 3'
Carbazole dioxazine violet, PV 23 date of appearance 1928 date of production 1953	blue dye emitted from edges time = 0', then dissolves to blue/green solution, time = 15'	solid dark green, time = 0'	no change
Hansa-yellow G, PY 1 date of appearance 1909 date of production 1910	solid turns yellow/orange time = 0'	no change	solid turns dark blue, time = 0'

Bibliography

1. Spengeman, W.F; Quinacridone pigments, Journal of Paint and Varnish Production, August 1970, p. 37.
2. Levison, H.W.; Pigmentation of Artists' Colours, Pigment Handbook, volume 2, Applications and Markets, edited by Temple. C. Patton, John Wiley & Sons Inc, New York, 1973, p. 423-434.
3. Castle, D.A.; Pigment Analysis in the Forensic Examination of Paints, 2. Analysis of Motor Vehicle Paint Pigments by Chemical Tests, Journal of the Forensic Science Society, 1982; 2, p. 179-186.





## SUMMARY

There are very few authentic relics of early European printed textiles /13-14th century/ in museum collections. In the course of the investigations performed in the sixties it was found that the bulk of the previously published material were but fakes. In the collection of the Budapest Museum of Applied Arts there are some pieces claimed to belong to early printed textiles. Pigment material of these pieces was investigated by X-ray diffraction method. Evaluating the diffraction patterns, barium white could be detected as additive for a red and a green paint. This material is noted to be used, according to technical literature, since the beginning of the 19th century only. By two items claimed to be printed with silver it was found that metallic tin had been used instead of silver, in the case of a piece printed with "gold" it turned out to be decorated with copper. Substituting the two precious metals by tin and copper, respectively is not mentioned in technical literature on printed textiles. Further investigations on the textile support and the style are needed to decide on the authenticity of the pieces.

## X-RAY DIFFRACTION INVESTIGATION ON THE PIGMENTS OF PRINTED TEXTILES

Márta Járó and Ágnes Timár-Balázsy  
Conservation scientists  
National Centre of Museums  
Budapest 100, P.O.B. 54. 1476 Hungary

László Kriston  
Physicist  
Institute of Criminology  
Budapest, Maros u. 6/a. 1028 Hungary

Introduction

The decoration of textiles by printing with the help of printing blocks and pigment pastes evolved from hand painting of the textiles with a brush. In early textile printing practice the pigments /mostly inorganic ones/ coloured only the surface of the textile threads.

While the first evidences on printed textiles are known, according to authentic evidences, from Achim-Panopolis, Egypt /infant's tunic, white patterns on blue and printing blocks/, dated to 4-5th century A.D. /1/, the first authentic pieces of printed textiles of European origin are known from the 14th century /2/. The production technique for these pieces, however, testifies a fairly high level of technology that leads us to suppose some previous European practice /3/.

In the late 50-ies and the early 60-ies, D.King investigated more than 120 pieces of printed textiles /4/. From these, only 40 pieces were proved to be original, while the remaining considerable amount turned out to be 19th century fakes. These were classified in the publications of Forrer, a 19th century collector and expert on printed textiles, to the so-called Rhenish group, printed partly on silk /5,6/. King did not comment on the question whether Forrer was aware of the fact that the pieces studied by him were fakes or fell victim to clever forgery. The results of King's investigation diminished the number of evidences of old European printed textiles to quite a great extent. This quantity is very low, even if we add the Late Medieval printed textiles published by Leonie von Wilkens /7/.

In the collection of the Budapest Museum of Applied Arts there are some fragments of printed textiles claimed to be early ones /13th-15th centuries/, a part of which comes from the Forrer

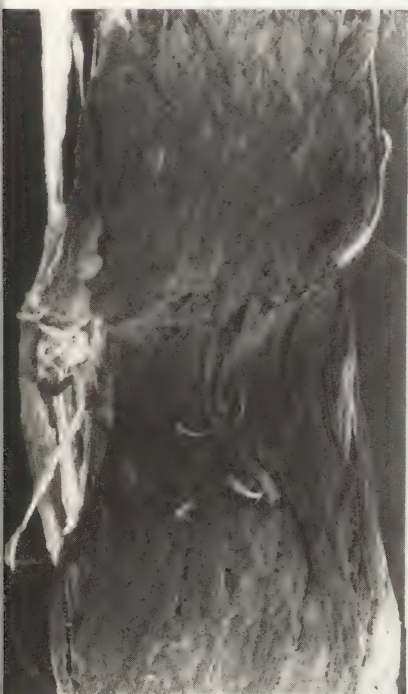


Fig.1: SEM of a thread from textile No.7289



Fig.2: Detail of the textile No.7289



Fig.3: German silver-shine printed textile No.7289



collection. In the light of the above considerations, the possibility of forgery emerged. The art historian in charge of the textiles requested a scientific investigation for the study of this problem. 6 pieces were investigated by X-ray diffraction method, using Debye-Sherrer camera technique. According to our present knowledge this method has not been used yet for the authenticity studies of printed textiles, based on the identification of the pigments, in spite of the fact that X-ray diffraction proved to be useful in the study of pigments and in connection of that, in the dating of painted objects.

#### Contemporary written sources on pigments used in textile printing

In connection with the pigments used for the production of printed textiles, there are very scanty pieces of information in contemporary written records. There are two works registered in relevant technical literature: that of Cennino Cennini, entitled "Trattato della Pittura", and the manuscript of a formulary from the St. Catharina monastery of Nuremberg /8/. Based on the data of these two 15th century sources, the following pigments were mixed in a pigment paste of linseed oil for the printed textiles:

white: white lead

red: minium, cinnabar, red ochre

green: verdigris

blue: ultramarine blue

yellow: orpiment,

as well as organic dyes mixed with chalk, white lead or calcined egg shells, like indigo, Brasil wood.

Apart from these gold and silver were also used.

The above materials are identical with ones generally used for contemporary painting.

There were no analytical data on the pigments of 13-15th century printed textiles at our disposal.

#### Experimental

For more precise characterization of inorganic compounds, their metallic ions /mainly in the case of the identification of mordants/ X-ray fluorescence analysis is frequently practised /9,10,11/, however, some other means of analysis like optical emission spectroscopy, atomic absorption spectroscopy and microprobe analysis have also been reported /12,13,14/. All these methods are suitable for the study of the elementary composition, but the inorganic pigment cannot be identified unambiguously on the basis of such data. Starting from this perception we used the X-ray diffraction method for the identification of the pigments.

#### Preparing the samples

The paint layer was placed, together with the thread, into a 0,3 mm diameter Lindemann glass tube, because it was impossible to detach the pigment from the thread. Threads of 2-5 mm length were used for the analysis. The samples were irradiated in a Debye-Sherrer camera.

In the course of trial examinations it was found that the characteristic spectra of the material of the textile, that was identified by microscopical inspection as linen in all cases, is always present on the X-ray diffraction pattern, so we performed a control measurement on paintless linen as well /Fig. 4a./

#### Results

In Table 1 we give the inventory data and the results of X-ray diffraction analysis of investigated textiles.

#### Conclusion

Based on the results of the X-ray diffraction analysis, we can state the following:

The two red pigments analysed, cinnabar and red bole, were known and used at the period claimed. Barium white beside the red bole in sample 2, however, was used in painting only after the beginning of the 19th century according to technical literature. This fact does not exclude the possibility that powdered barite was mixed to the pigment paste earlier.

The light green pigment could not be identified, the barium white appears in the sample /similar to sample 2/.

Interesting and unexpected results were obtained from the analysis of samples claimed to be ornamented with gold and silver. We have found no references for substituting these precious metals with copper and tin, as found in this case, for printed textiles. Comparative data are needed to decide whether this fact means a



forgery or it was a common practice in medieval textile printing. This latter hypothesis might prove acceptable, for printed textiles were mainly used by lower classes imitating expensive gold and silver brocades. Costs of production might have been reduced by substituting gold with copper and silver with tin. Further investigations on the textile support and the style are needed to decide on the authenticity of the pieces.

Table 1: Results of investigation

Data in inventory record	XRF analysis results
1. No. 7275 German make of the 13th century; Red patterns in black circles on grey base.	Red colour by HgS, cinnabar /Fig. 4b./
2. No. 7287 German make of the 13th century; /Rhenish/, printed red pattern on yellowish base; from the Forrer collection.	Red colour by $\text{Fe}_2\text{O}_3$ , hematite with kaolin and $\text{BaSO}_4$ , barite white. The mixture is possibly composed of red bole and barium white. /Fig. 4c./
3. No. 8486 German make of the 14th century; Light green patterns on pinkish base.	The component responsible for the green colour could not be identified, the mixture contains gypsum and barium white. /Fig. 4d./
4. No. 7289 12-13th century; Silver-printed pattern on dark blue base.	Silver coloured pigment is furnished by tin. /Fig. 4e./
5. No. 7282 German make of the 14th century; Silver-shine printed ornament on blue base; from the Forrer collection.	The metal on the thread supposed to be silver, proved to be tin, similar to sample 4.
6. No. 7284 German make of the 13th century; /Rhenish/, golden printed patterns on pinkish base.	The golden colour is furnished by copper. /Fig. 4f./



Fig.4: X-ray patterns of the samples: a/ paintless linen, b/ sample 1, c/ sample 2, d/ sample 3, e/ sample 4, f/ sample 6. Operating conditions: Cu K $\alpha$  radiation, Ni filter, 40 kV, 60mA; diameter of the Debye-Scherrer camera: 114,6 mm, exposure: 3 hours, emulsion: Agfa Gevaert D7

### Acknowledgement

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### References

1. CIBA - Rundschau 24, Basel, April, 1938, p.856.
2. King, Donald: "Textiles and the Origin of Printing in Europe", Pantheon 20, 1962, p.30.
3. Ibid., p.30.
4. Ibid., pp.23-30.
5. Forrer, Robert: Die Zeugdrucke der byzantinischen, romanischen, gothischen und spätern Kunstepochen, Strassburg, 1894
6. Forrer, Robert: Die Kunst des Zeugdrucks vom Mittelalter bis zur Empirezeit, Strassburg, 1898
7. Wilckens, Leonie von: Der spätmittelalterliche Zeugdruck nördlich Alpen, Anzeiger des Germanischen Nationalmuseums, Nürnberg, 1983, pp.7-18.
8. Ploss, Emil, Ernst: Ein Buch von alten Farben, Impuls Verlag Heinz Moos, Heidelberg, Berlin, 1962, pp.94-95.
9. Masschelein-Kleiner, Lilien, Maes, Luc: "Ancient dyeing techniques in Eastern Mediterranean regions", ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb, 1978. 9/3
10. Dalrympe, H.E.: "Dye identification at the National Museum of Antiquities of Scotland", Dyes on historical and archaeological textiles - summary of talks, 2nd meeting, National Museum of Scotland, September 1983, pp.5-6.
11. Skelton, Maruta, Lee-Whitman, Leanna: A Systematic Method for Differentiating Between 18th Century Painted-Printed Chinese and Western Silks, Advances in chemistry series 212, Historic Textile and Paper Materials, Conservation and Characterization, University of California, 1984, pp.131-151.
12. Masschelein-Kleiner, Lilien, Znamensky-Festraets, N., Maes, Luc: "Les colorants des tapisseries tournaisiennes a XVe siecle. Étude comparative de trois fragments de la bataille de Roncevaux", Bulletin de l'IRPA. X-1967/68, p.133.
13. Torini, C.: "Atomic absorption spectrophotometry in the textile chemistry laboratory", Tinctoria 75 /1978/, pp. 160-162.
14. Koestler, R.J., Sheryll, R., Indictor, N.: "Identification of dyeing mordants and related substances on textile fibers: A preliminary study using energy dispersive X-ray spectrometry", Studies in Conservation, Vol.30, Numb.2, 1985, pp. 58-62.



## SUMMARY

Chemical composition of Chinese coins recovered from wrecked ships near the seabed of Shinan in the southern part of the Korean Sea, miscellaneous brass and glass antiques excavated so far, and porcelain sherds classified by their regional origins were investigated by several research organizations and universities. In this article, major analytical data obtained through this research were presented and cluster analysis, principal composition analysis, and relevant statistical methods of evaluating these data were discussed with special regards to their archeological origin, age, and other technological factors. A multivariate statistical method was introduced for Korean porcelain sherds as the reference datum.

## CHEMICAL COMPOSITION OF PORCELAINS, CHINESE COINS, BRASS AND GLASSY ANTIQUES EXCAVATED IN KOREA

You Sun Kim\*

Committee of Cultural Property, Ministry of Culture & Public Information, Republic of Korea, Seoul, Korea

## 1. Introduction

Recent developments of analytical technology in the fields of atomic absorption spectrometry, radio-activation analysis, plasma emission spectrometry, and others had made it possible to analyse multicomponents of an archeological sample together with its trace compositions. Various approaches to evaluate the analytical data obtained were reported for Chinese coins and imitated coins (1)(2)(3)(4) in order to identify the age, origin, and technological characteristics. Mathematical and statistical approaches to develop an efficient method of evaluating the analytical datum had also been reported (5)(6)(7)(8)(9).

In this country, porcelains of aged, imitated, and modern arts had been found or excavated in many areas and archeologists or historians had usually been concerned with identifying these on basis of physical observations of their morphological, design, and other physical features. However, these identifications had ignored the geological characteristics of materials, technological features, and other essential scientific data, and hence they made many mistakes or misjudgements, which resulted in serious confusion concerning their origin, age, and relevant archeological values. Data on the concentration of Na, K, Sc, Cr, Fe, Co, Cu, Ga, Rb, Cs, Ba, La, Ce, Sm, Eu, Tb, Lu, Hf, Ta, and Th obtained by neutron activation analysis (10)(11)(12) have, therefore, been used to characterise Korean porcelain sherds by multivariate analysis. The mathematical approach employed is Principal Component Analysis (PCA). PCA was found to be helpful for dimensionality reduction and for obtaining information. This method had revealed that porcelains analysed by this approach could well be applicable for identifying the regional origin of the sample, if a sherd of that porcelain is available.

A large quantity of Chinese coins were recovered at the seabed of Shinan area in the southern part of the Korean Sea and it was considered worthwhile to analyse these coins for their chemical composition and to investigate the analytical data by those methods described above (14). Furthermore, there were Korean bronze and glassy antiques excavated in the Kyungju area and other historical remains, and the origin, age, and other archeological features had been under serious discussion. Analysis of chemical composition of these relics was also conducted and an attempt was made to evaluate the analytical data to identify their origin and age (20).

In this article, studies on porcelains, Chinese coins, Korean brass and glass relics were described according to their chemical composition and future prospects for these approaches in archeological study of Korean relics were discussed.

## 2. Porcelains\*\* (13)

84 samples of porcelain sherds collected from porcelain production sites in South Korea were analysed for their concentration of chemical elements such as Na, K, Sc, Cr, Fe, Co, Cu, Ca, Rb, Cs, Ba, La, Ce, Sm, Eu, Tb, Lu, Hf, Ta, and Th by means of radio-activation analysis. The obtained analytical data (10) were further evaluated through principal component analysis method. (8)(9). Elements of Na, K, Fe, and Ba were found that they contributed significantly to principal components of 1,2,3, and 4, respectively. Trace elements of Cu, Ga, La, Ce, Th, Cr, Hf, Cs, Sc, and Co were also found that they contributed to principal components of ten as listed in the table 1. These ten elements were chosen for pattern recognition analysis (10). The calculated data of this analysis were treated to obtain VC Matrix (10x10) value S and ten eigenvalues were calculated as shown in the table 1. Eigenvector coefficients, communality, and percentage of variance accounted for in principal components of 1,2, and 3 were calculated. Finally, PCA plots were made as shown in Fig.1 and Fig.2 on

\* Also working at the Korea Advanced Energy Research Institute, P.O. Box 7, Daeduk Danji, Chungnam, Korea.





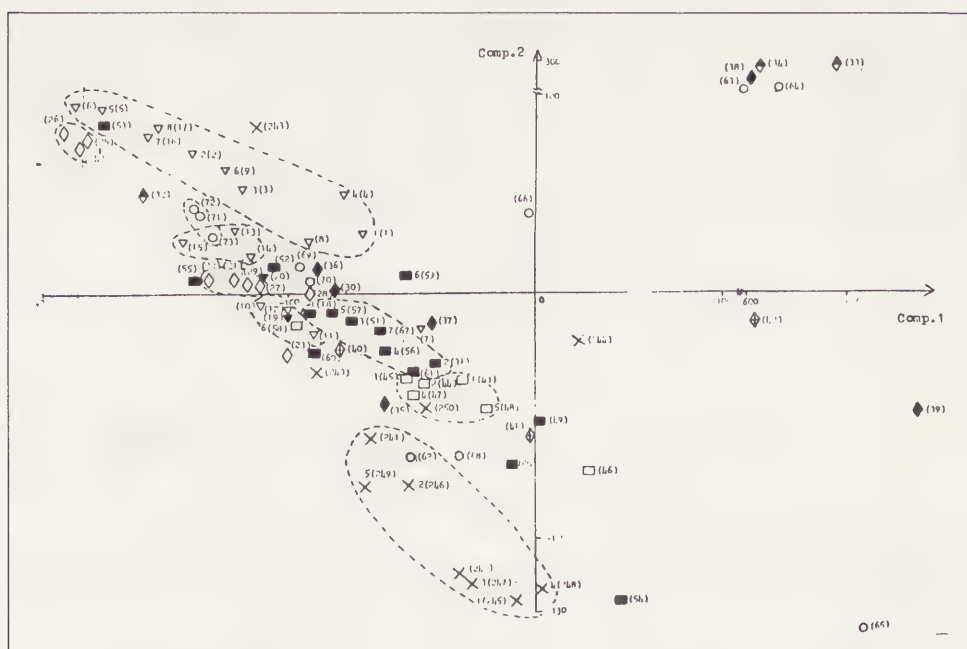


Fig.1 Plot of PCA 1 and 2.

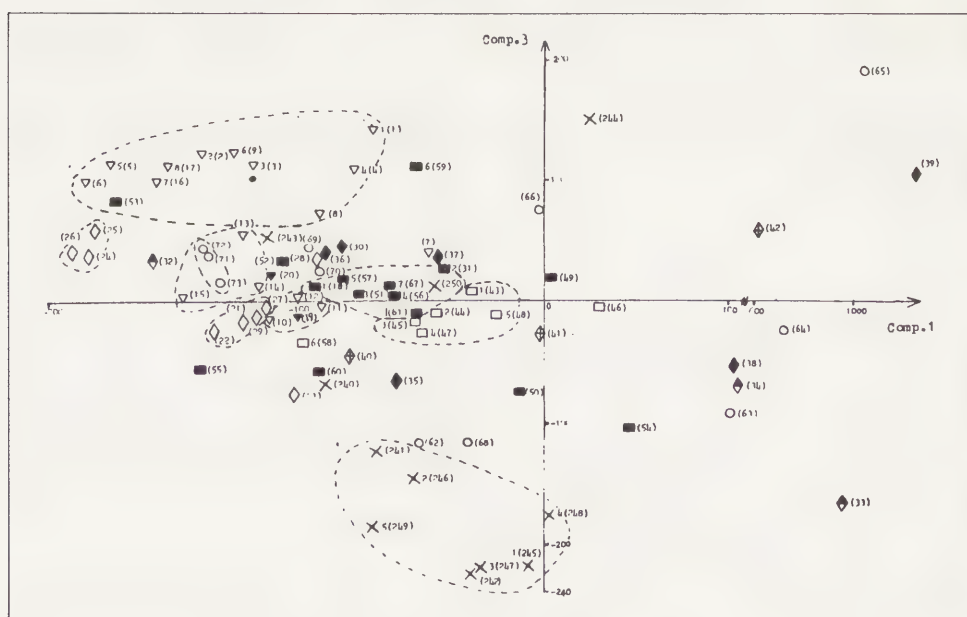


Fig.2 Plot of PCA 1 and 3.

detailed study of their chemical compositions. Fortunately, a large quantity of Chinese coins were recovered from the southern sea bed of this country and the following analytical study on chemical compositions of these coins could possibly extend an understanding of the existing data a great deal.

Atomic absorption spectrophotometer was used for analysing the 10 elements (Cu, Pb, Sn, Zn, Sb, Fe, Ag, Co, Ni, and Mn) on 64 coins and they were classified into 8 groups depending on their chemical compositions as shown in table 4. The nomenclature observed on the surface of each coin indicating the area in which that coin was found was listed in table 5. Lead and tin compositions of coins of each group were summarised in Fig.3 comparing with the previous results obtained by other workers. (1-4) The results show that Cu, Pb, and Sn were found to be major elements present in the coin and its composition ratio was averaged 6 to 2 or 1. The composition of trace elements on coins was classified at 3 levels: Sb, Fe, and Zn (0.02-2.2%) Ag, Ni, and Co (50 ppm-5500 ppm) and Mn (Trace). The amount of major elements Cu and Sn were decreased while increased in Pb by the passage of ages (10th-13th Century) in China. There seemed to be no systematic compositional change in major elements, but contents of trace elements were confirmed to increase with age.

Table 3. Chemical Composition\* of Shinan Coins

Nomenclature & Age of Issuing	Element									
	Cu (%)	Pb (%)	Sn (%)	Sb (%)	Zn (%)	Fe (%)	Ni (PPm)	Ag (PPm)	Co (PPm)	Mn (PPm)
1. Ohju Chun (B.C 118-A.D 581)	8.29	6.4	6.8	0.306	0.039	0.508	988	1,650	320	T
2. Ohju Chun (B.C 118-A.C 581)	79.9	10.8	5.9	0.700	0.080	0.952	1,438	1,340	1,910	83
3. Kaewon Tongbo (621)	63.7	14.4	14.7	0.313	0.082	0.544	810	1,085	323	T
4. Kaewon Tongbo (814-847)	71.7	5.3	20.0	0.328	0.259	0.797	1,310	5,045	4,233	T
5. Kaewon Tongbo (758-760)	66.3	18.2	12.1	0.217	0.160	1.402	1,290	638	860	70
6. Kunwon Chungbo (750-760)	72.7	10.0	7.0	0.323	0.175	1.396	1,248	2,115	893	58
7. Dankuk Tongbo (959)	69.2	19.3	11.2	0.332	0.039	0.226	790	978	395	143
8. Songwon Tongbo (968-975)	57.5	26.0	13.8	0.167	0.028	0.202	718	2,100	375	T
9. Taepyung Tongbo (976-983)	61.5	19.6	18.6	0.384	0.442	0.265	1,070	1,175	370	n.d.
10. Sunwha Wonbo (990-994)	59.5	17.2	18.6	0.254	0.450	0.166	810	1,330	272	n.d.
11. Chido Wonbo (995-999)	64.5	21.7	6.3	0.136	0.147	0.245	690	1,838	210	T
12. Hampuung Wonbo (998-1003)	66.7	20.8	9.8	0.160	0.048	0.155	435	953	140	T
13. Sangpu Wonbo (1008-1016)	63.3	23.1	11.4	0.032	0.038	0.224	408	425	113	T
14. Sang Pu Tongbo (1008-1016)	62.8	21.6	11.6	0.083	0.020	0.224	660	327	T	n.d.
15. Chunsong Wonbo (1023-1031)	63.2	20.6	12.9	0.252	0.051	0.215	685	575	T	n.d.
16. Chunsong Wonbo (1023-1031)	65.4	20.8	15.2	0.308	0.029	0.191	615	485	245	T
17. Myungdou Wonbo (1032-1033)	69.6	16.1	14.2	0.085	0.027	0.274	505	1,220	T	T
18. Kyungwu Wonbo (1034-37)	65.1	20.3	13.8	0.253	0.361	0.190	333	730	T	n.d.
19. Kyungwu Wonbo (1034-1037)	58.9	14.9	6.8	0.137	0.176	0.384	307	150	97	T
20. Hwangsong Tongbo (1038-1040)	63.5	23.9	9.6	0.269	0.234	0.215	300	233	90	T



Table 3. (Continued)

21. Whangsong Tongbo (1038-40)	65.6	20.9	11.6	0.123	0.038	0.243	410	1,230	T	n.d.
22. Kyungryouk Chungbo (1041-48)	75.5	13.8	9.6	0.079	0.035	0.368	575	1,113	323	T
23. Chiwa Wonbo (1054-55)	63.9	22.6	6.8	0.169	0.028	0.190	383	573	T	T
24. Gawoo Tongbo (1056-63)	64.9	21.6	9.9	0.301	0.118	0.311	328	728	T	n.d.
25. Kawoo Tongbo (1056-63)	72.8	11.5	14.2	0.081	0.291	0.288	280	2,943	128	T
26. Chipyeong Wonbo (1004-67)	67.0	17.9	11.9	0.093	0.108	0.269	580	385	78	n.d.
27. Chipyeong Wonbo (1064-67)	63.2	20.9	11.0	0.110	0.080	0.121	150	288	T	n.d.
28. Chipyeong Tongbo (1064-67)	65.4	19.3	11.3	0.152	0.161	0.154	423	310	200	T
29. Hinyung Jungbo (1068-77)	64.8	23.1	11.1	0.063	0.127	0.299	T	360	208	T
30. Hinyung Wonbo (1068-77)	70.1	21.0	11.0	0.211	0.301	0.359	313	538	T	T
31. Wopung Tongbo (1076-85)	59.9	23.9	10.7	0.162	0.076	0.227	500	298	165	63
32. Wopung Tongbo (1078-85)	68.1	22.5	11.8	0.249	0.040	0.265	577	227	T	n.d.
33. Wonwu Tongbo (1086-93)	61.2	22.2	11.5	0.112	0.306	0.235	153	190	T	n.d.
34. Sosung Wonbo (1094-97)	66.8	21.4	7.9	0.132	0.260	0.399	450	1,170	217	107
35. Sosung Wonbo (1094-97)	69.2	23.7	9.3	0.251	0.097	0.320	720	873	T	n.d.
36. Wonbu Tongbo (1098-1100)	62.4	23.1	13.0	0.072	0.097	0.270	453	475	285	T
37. Sungsong Wonbo (1101)	70.5	23.0	6.5	0.300	0.066	0.235	335	420	170	n.d.
38. Sungsong Wonbo (1101)	63.6	24.3	10.2	0.084	0.067	0.219	130	480	358	T
39. Soungyung Chungbo (1102-06)	62.2	18.5	26.4	0.075	0.029	0.299	340	368	205	n.d.
40. Sungyung Tongbo (1102-06)	60.8	27.4	11.3	0.460	0.319	0.567	465	1,613	73	n.d.
41. Daekwan Tongbo (1107-1110)	65.4	24.5	9.5	0.160	0.407	0.425	488	915	165	T
42. Chunghwa Tongbo (1111-17)	65.0	22.6	7.4	0.273	0.272	0.727	543	593	80	T
43. Chunghwa Tongbo (1111-17)	63.3	21.9	12.0	0.123	0.203	1.141	523	758	193	n.d.
44. Chunghwa (1111-17)	64.3	22.2	8.1	0.327	0.070	0.257	593	360	T	T
45. Sunhwa Tongbo (1119-25)	58.1	29.7	9.2	0.220	0.122	1.583	533	628	253	n.d.
46. Sunhwa Tongbo (1119-25)	66.7	25.1	5.7	0.092	0.064	1.222	333	260	T	n.d.
47. Sunhwa Tongbo (1119-25)	66.2	21.8	12.0	0.141	0.135	0.303	368	408	295	n.d.
48. Sunhwa Tongbo (1119-25)	71.3	4.4	22.1	0.030	0.030	1.062	630	1,155	T	T
49. Kunyum Tongbo (1127-30)	57.4	21.8	12.4	0.128	0.132	1.372	383	503	500	T
50. Kunyum Tongbo (1127-30)	56.4	21.2	13.5	0.147	0.289	0.662	335	630	235	T
51. Sohung Tongbo (1131-62)	60.5	25.4	11.9	0.172	0.171	0.676	553	828	T	n.d.
52. Sohung Wonbo (1131-62)	64.2	21.5	14.8	0.097	0.042	1.677	667	257	130	57
53. Sohung Wonbo (1131-62)	56.4	29.9	8.6	0.146	0.353	1.010	465	238	88	T

Table 3. (Continued)

54. Sunhi Wonbo (1174-89)	59.6	30.8	2.9	0.226	0.062	0.936	250	1,097	167	T
55. Sunhi Wonbo (1174-89)	55.9	28.2	8.7	0.269	0.182	2.138	878	450	245	T
56. Chungryung Wonbo (1156-60)	66.8	5.1	20.4	0.138	0.153	0.929	413	733	113	T
57. Daechung Tongbo (1175)	69.4	7.4	18.5	0.247	0.150	0.632	827	817	547	n.d.
58. Sohi Wonbo (1190-94)	58.7	33.6	2.9	0.272	0.084	1.146	523	990	393	n.d.
59. Kyungwon Tongbo (1195-1200)	58.3	33.0	3.3	0.116	0.135	1.118	808	675	195	T
60. Katai Tongbo (1201-04)	57.6	29.8	3.6	0.150	0.286	1.525	783	1,170	593	n.d.
61. Kaehi Tongbo (1205-1207)	56.1	32.2	3.5	0.124	0.238	1.843	527	2,197	310	n.d.
62. Kachung Tongbo (1208-24)	59.8	30.1	3.0	0.201	0.080	1.502	925	473	163	T
63. Kyungchung Wonbo (1260-64)	58.4	31.5	3.5	0.133	0.149	1.397	700	530	T	T
64. Chunha Taipyung (After Dang Song Dynasities)	0.43	13.6	91.2	0.547	0.055	0.424	270	90	T	n.d.
Total mean (64 coins* of 46 kinds)	63.5	21.0	12.2	0.201	0.147	0.627	567	876	280	T

Remarks. T: Trace, n.d.: Non Detectable.

\* Each coin was divided in 4 places where samples for analysis were taken. The analytical value for a coin shown in this table was the mean of 4 data of analysis of the coin.

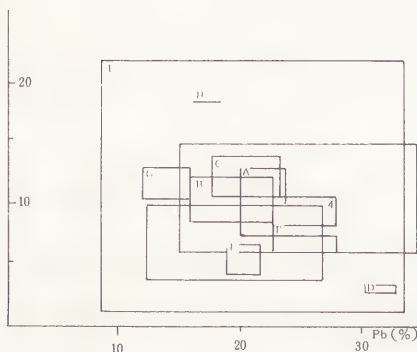


Fig.3 Lead and Tin Compositions of Coins

1. The present results of Shinan Coins.
2. Results obtained by H. Mabuchi.<sup>(1)</sup> (1978)
3. Results obtained by Y. Sano.<sup>(2)</sup> (1982)
4. Results obtained by M. Misugami.<sup>(15)</sup> (1973)

Table 4. Chemical Compositions of Coins Classified by their Groupings

Group Comp.	A	B	C	D	E	F	G	H
Cu (%)	64.6 $\pm$ 2.8	64.0 $\pm$ 3.4	60.7 $\pm$ 3.2	58.4 $\pm$ 1.2	63.0 $\pm$ 5.3	69.2 $\pm$ 1.8	72.6 $\pm$ 2.4	60.5 $\pm$ 1.2
Pb (%)	21.9 $\pm$ 1.9	19.3 $\pm$ 3.4	20.5 $\pm$ 2.9	31.6 $\pm$ 1.3	25.1 $\pm$ 3.0	5.6 $\pm$ 1.3	13.8 $\pm$ 1.9	18.4 $\pm$ 1.2
Sn (%)	11.4 $\pm$ 1.6	10.2 $\pm$ 2.1	12.2 $\pm$ 1.6	3.2 $\pm$ 0.3	7.1 $\pm$ 1.1	20.3 $\pm$ 1.5	12.7 $\pm$ 2.1	18.6
Sb (%)	0.173	0.217	0.166	0.175	0.185	0.138	0.081	0.319
Zn (%)	0.074	0.296	0.174	0.148	0.140	0.111	0.117	0.446
Fe (%)	0.235	0.347	1.120	1.352	0.840	0.874	0.310	0.216
Ni (ppm)	477	314	505	578	514	727	453	940
Ag (ppm)	613	692	599	1,019	630	901	1,759	1,253
Co (ppm)	142	77	199	260	119	220	150	321
Mn (ppm)	T	T	T	T	T	T	T	n.d.

Table 5. Shinan Chinese Coins Classified by Grouping

## Group A. 20 Coins

* No.7	Dankuk Tongbo	(959)	No.8	Songwon Tongbo	(968-975)
No.12	Hampyung Wonbo	(998-1003)	No.13	Sangpu Wonbo	(1008-1016)
No.14	Sangpu Tongbo	(1008-1016)	No.15-16	Chunsong Wonbo	(1023-1031)
No.20	Hwangsong Tongbo	(1038-1040)	No.24	Gawoo Tongbo	(1056-63)
No.26-27	Chipyung Wonbo	(1064-67)	No.28	Chipyubg Tongbo	(1064-67)
No.29	Hinyung Jungbo	(1068-77)	No.31-32	Wonpung Tongbo	(1078-85)
No.35	Sosong Wonbo	(1094-97)	No.36	Wonbu Tongbo	(1098-1100)
No.38	Sungsong Wonbo	(1101)	No.44	Chunghwa Tongbo	(1111-1117)
No.47	Sunhwa Tongbo	(1119-1125)			



Table 5. (Continued)

## Group B. 8 Coins

No.18-19	Kyungwu Wonbo	(1034-37)	No.21	Whangsong Tongbo	(1038-40)
No.30	Hinyung Wonbo	(1068-77)	No.33	Wonwu Tongbo	(1086-93)
No.34	Sosung Wonbo	(1094-97)	No.44	Sungnyung Tongbo	(1102-06)
No.41	Daekwan Tongbo	(1107-1110)			

## Group C. 7 Coins

No.42-43	Chunghwa Tongbo	(1111-1117)	No.45	Sunhwa Tongbo	(1119-1125)
No.49-50	Kunyum Tongbo	(1127-30)	No.51	Sohung Tongbo	(1131-1162)
No.52	Sohung Wonbo	(1131-1162)			

## Group D. 7 Coins

No.54	Sunhi Wonbo	(1174-1189)	No.58	Sohi Wonbo	(1190-94)
No.59	Kyungwon Tongbo	(1195-1120)	No.60	Katai Tongbo	(1201-04)
No.61	Kaehi Tongbo	(1205-1207)	No.62	Kachung Tongbo	(1208-24)
No.63	Kyungchung Wonbo	(1260-64)			

## Group E. 6 Coins

No.11	Chido Wonbo	(995-999)	No.23	Chihwa Wonbo	(1054-55)
No.37	Sungsong Wonbo	(1101)	No.46	Sunhwa Tongbo	(1119-1125)
No.53	Sohung Wonbo	(1131-62)	No.55	Sunhee Wonbo	(1174-89)

## Group F. 3 Coins

No.48	Sunhwa Wonbo	(1119-1125)	No.56	Chungryung Wonbo	(1156-1160)
No.57	Daechung Tongbo	(1175)			

## Group G. 3 Coins

No.17	Myungdou Wonbo	(1032-33)	No.22	Kyungryouk Chungbo	(1041-48)
No.25	Kawou Tongbo	(1056-63)			

## Group H. 2 Coins

No.9	Taepyung Tongbo	(976-983)	No.10	Soonhwa Wonbo	(990-994)
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## Others 8 Coins

No.1-2, Ohju Chun, No.3-5, Kaewon Tongbo, No.6, Kunwon Chnwon Chungbo, No.39, Soungnyung Chungbo (1102-06), and No.64, Chunha Taipyung (after Dang-Song Dynasties)

\* Sample numbers are referred to the table 3.

## 4. Brass Antique

Chemical composition of brass antiques excavated in the southern part of Korea, which had been excavated in sherds' style in many cases, had been considered to have wide variations, more than those of in the case of coins due to metallurgical differences between each sample with different origins of usage. Studies on brass antiques, which had been excavated in a definite shape of the original design, had been conducted in order to investigate the general trend of the main composition, which may be helpful to identify the origin of relics or sherds excavated. In table 6, analytical data of 10 typical antiques obtained by means of atomic absorption spectrometry were shown. By examining the data, it was found that the Cu content could roughly be classified in three levels : 79-80%, 66-72% and 56-66%. These levels were further examined for their tin and lead compositions as shown in Fig.4, which had been known as the main composition of ancient oriental bronze alloy. Samples numbered 1,2, and 3 or 7 and 5 showed some resemblance to each other. In fig.5, zinc and tin compositions were summarized which could show clearer features in samples 1 and 3 and samples 7 and 5. According to Mr. Chun, (16) zinc had been one of the essential components of the ancient oriental bronze alloys, but due to the volatility of the zinc (b.pt. 950°C), it was very difficult to maintain zinc in bronze composition during the alloying process (ca. 1000°C or more). Some cases of low zinc content in Japanese bells had previously been reported. (17) Even though the number of samples studied were not enough to be classified in this trend of Korean bronze antiques of high and resembled zinc composition, I believe that further extensive studies on this line would result in a significant break through in Korean style ancient bronze antiques in this region of eastern Asia.

Table 6. Major Chemical Components Found in Bronze Samples Excavated in Korea. (19)

Sample No.	Type of Relics	Age (Estimated)	Cu	Major Sn	Components (%)		Remarks
					Pb	Zn	
1	Printing Type	15C. AD	79.45	13.20	1.66	2.30	
2	Bronze Coin	11C. AD	65.7	13.88	2.35	18.0	
3	Temple Bell	9C. AD	80.10	12.20	5.38	2.18	
4	Bronze Bell	BC. 1-2	51.49	26.10	6.72	1.09	
5	Anup Pond's Relics	9-8C. AD	66.0	2.36	0.54	30.0	
6	Whungnam Tomb's Bronze Bell	5-6C. AD	70.4	6.9	4.04	trace	
7	Chunma Tomb's Bronze Pieces	6 C. AD	62.2	1.4	-	25.9	
8	Hwangryongsa Temple's Relics	10-8C. AD	72.2	20.7	0.49	0.02	
9	"	"	66.1	17.7	-	0.03	
10	"	"	56.0	26.7	-	trace	

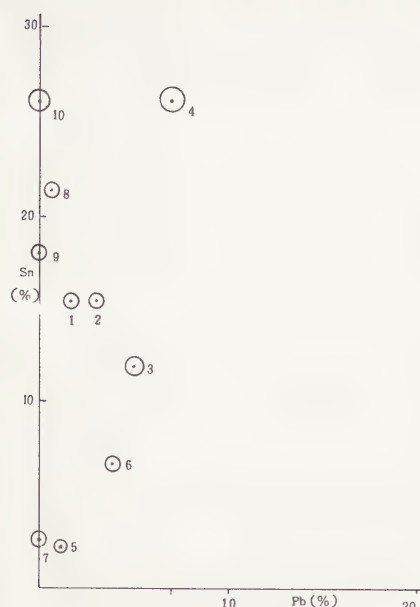


Fig.4 Lead and Tin Compositions of Korean Bronze.

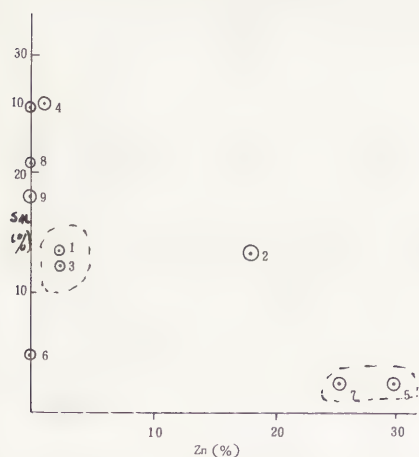


Fig.5 Zinc and Tin Compositions of Korean Bronze

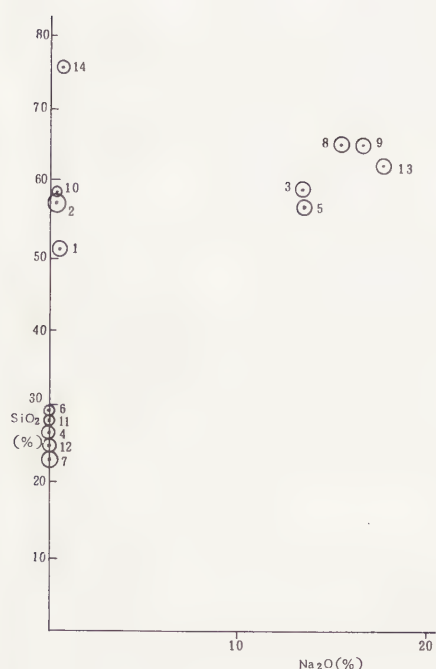


Fig.6 Silica and Sodium Oxide Compositions of Glassy Relics Excavated in Korea.

## 5. Glassy Relics

In table 7, analytical data of glass bead (Magatama shaped), glass ornaments, and other glassy sherds excavated were shown which were obtained by emission spectrometry and atomic absorption spectrometry. Japanese data(18) were also shown as comparative data. There are roughly three kinds of silica content : 23-29.6%, 50-57.5%, and 58-65%. The silica and sodium composition of samples were shown in fig.8, which indicated that there were two kinds of sodium style glass. In fig.7, silica and lead oxide compositions were shown, which indicated that there were two kinds of lead glass. In fig.8, silica and aluminum oxide compositions were shown which indicated that two kinds of sodium glass and two kinds of lead glass existed in the glassy relics studied.

Table 7. Major Chemical Components of Glassy Relics Excavated in Korea (19)

Sample No.	Type of Relics	Age (Estimated)	Major SiO <sub>2</sub>	Components (%)			Remarks
				Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	PbO	
1	Hwangryongsa Temple's Glass Bead Relics	10-8C. AD	50.7	0.18	0.06	47.50	
2	"	"	56.8	0.17	0.15	41.80	
3	"	"	58.1	15.90	13.50	0.09	
4	"	"	25.8	0.04	trace	72.90	
5	"	"	59.6	1.60	13.30	0.30	
6	"	"	29.6	0.02	trace	69.20	
7	"	"	23.0	0.02	trace	75.60	
8	Whangnam Tomb's Glass Bed (Silla Dynasty)	6 C. AD	65.0	5.94	14.9	0.2	
9	"	"	65.4	5.85	15.3	0.1	
10	Anup Pond's Glass Bead	6-7C. AD	57.5	0.16	0.03	40.6	
11	*Glasses (Yakushiji, Nara, Japan)	8 C. AD	28.0	0.06	-	66.0	
12	*Glasses (Shosoin Repository, Japan)	8 C. AD	24.7	0.31	0.12	71.9	
13	*Bluish Green Magatama (Otani-Wakayama, Japan)	3-6C. AD	62.4	7.75	16.3	trace	
14	*Ihiyama Round Bead (Blue) (Japan)	3-6C. AD	74.6	5.42	1.38	trace	

\* After K. Yamaskai, "Tenth International Congress on Glass." (9-15 July., 1974, Kyoto, Japan)



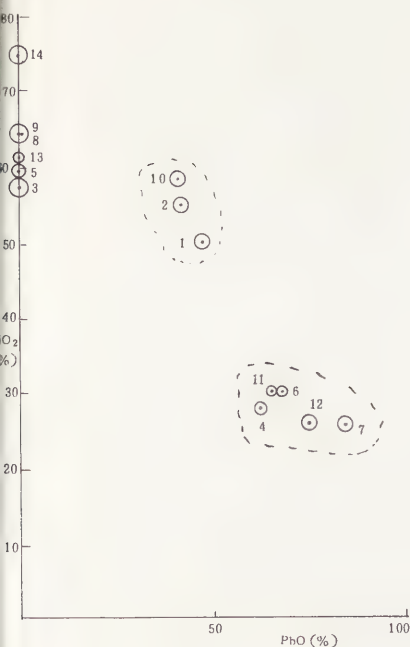


Fig.7 Silica and Lead Oxide Compositions of Glassy Relics Excavated in Korea.

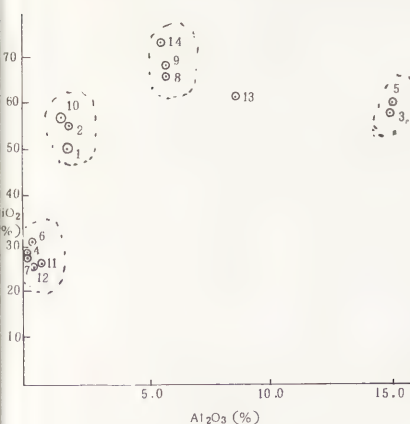


Fig.8 Silica and Aluminum Oxide Compositions of Glassy Relics Excavated in Korea.

Glassy materials are usually composed of natural geological pure materials without being processed at such high temperatures as bronze and other alloys and chemical composition of these relics depended mostly on regional geological characteristics of raw materials, which may not be significantly differentiated from each other. However, resemblances found between Korean and Japanese relics and two kinds of sodium or lead glasses classified by this method are quite interesting.

## 6. Conclusion

Results described in this article should further be studied and interpreted as far as history of art and technique are concerned. However, analytical data of composition of relics found in Korea may, in future, be able to contribute to understand the general trend of history of art and technique in this region of Asian countries.

## References

1. H. Mabuchi, et al., "Analysis of Chemical Compositions of Oriental Aged Coins by Atomic Absorption Analysis." Kobunkasai Kakaku 22 20 (1978, Tokyo Japan).
2. Y. Sano and K. Dominaga "Study on the deviations of chemical component in Chinese aged coins." Ibid. 27 12 (1982, Tokyo, Japan).
3. Y. Sano, K. Nosu, and K. Tominaga, "Study on chemical compositions of aged coins by multivariate methods." Ibid. 28 44 (1983, Tokyo, Japan).
4. R. Hirao et. al., "Chemical compositions of coins in Chenkan Dynasty." Ibid. 29 27 (1984, Tokyo, Japan).
5. M.J. Karson, "Multivariate Statistical Methods." Iowa State Univ., Press (1982).
6. K. Varmuza, "Lecture Notes in Chemistry." Pattern Recognition in Chemistry. New York (1980).
7. D.N. Lowley and A.E. Maxwell, "Factor Analysis as a Statistical Method." Butterworths, London (1983).
8. J. Arunachalam and S. Gangadharan, *Analytica Chimica Acta* 157 245 (1984).
9. Indem, J. *Indian Acad. Forensic Sci.* 20 54 (1981).
10. C. Lee, O.C. Kwun, N.B. Kim, and I.C. Lee, *Bulletin of Korean Chem. Soc.* 6 241 (1985).
11. C. Lee, N.B. Kim, I.C. Lee, and K.S. Chung, *Talanta* 24 241 (1977).
12. C. Lee, *J. Kor. Nucl. Soc.* 5 137 (1973).
13. H.T. Kang and C. Lee, *Conservation Science* 6 122 (1985, National Research Institute of Cultural Property, Bureau of Culture Property, Seoul, Korea).
14. C.K. Lee, D.I. Kang, and C.K. Hwang, Ibid. 6 135 (1985).
15. M. Misugami, "Metallic compositions of aged coins recovered at Shikaidai" Report of the city museum of Hakodate, 1973 p.20-32.
16. S.U. Chun, "The history of sciences in Korea." p.275 (1966, Seoul, Korea).
17. U. Nakakuchi, "Archeology of Cupper." Tokyo (1972).
18. K. Yamasaki, *World Archeology Series Vol.16* p.132, Tokyo (1962) and Tenth International Congress on Glass. (9-15, July, 1974, Kyoto, Japan).
19. Y.S. Kim et. al., "International Symposium on the Conservation and Restoration of Cultural Property," p.170-191 (Tokyo National Research Institute of Cultural Property, 1979, Tokyo, Japan).





SUMMARY:

Recently art-historical dendrochronology was called into doubt. There were three main points of criticism: some reference chronologies were still floating, the provenance of wood in the panels of paintings was not known, and the estimation of the number of sapwood rings was uncertain. These three points can now be considered solved. The reference chronology for dating Flemish and Dutch paintings has been shifted by six years towards the present, the oak timber used for the backing of most of these paintings of the 15th to 17th century is of Polish and Baltic origin, and the sapwood allowance is 13 to 19 years, with 15 as the median. The consequences for dating the respective paintings are described.

NEW FINDINGS FOR THE DENDROCHRONOLOGICAL DATING OF PANEL PAINTINGS OF THE 15th TO 17th CENTURY

P. Klein\*, D. Eckstein\*, T. Wazny†, J. Bauch\*

\* Institute for Wood Biology, University of Hamburg, Leuschnerstr. 91, D-2050 Hamburg 80, FRG

† Academy of Fine Arts, Conservation Faculty, Wybremeze Kosciuszkwskie 37, 00-379 Warszawa, Poland

Introduction

Some 20 years ago dendrochronology was introduced into art history as a dating tool. A few years later the first results were published. That study dealt with paintings by the Dutch painter Philips Wouwerman who spent his entire life in Amsterdam (3, 5). The panels were successfully dated using the South German oak tree-ring chronology. At that time only three long oak chronologies were in existence for Central and Western Europe (8, 9), and a high similarity was found between the tree-ring series of the Wouwerman panels and the South German reference chronology. Since the 16th and 17th century portion of the chronology contained mainly timber from Hesse in central Germany, the panels were assumed to be from trees cut in the Hessian hills and transported to the Netherlands. It was important also to establish a likely range of felling dates and the possible time lapse between the felling of the tree and the creation of the painting. Many of the panels used by Wouwerman had some sapwood rings, so the felling dates of the oak trees were estimated with an allowance for sapwood of  $20 \pm 5$  years. This figure was derived by a statistical evaluation of some 500 oaks along both sides of the river Rhine (9). Thus the tree-ring series of the Wouwerman paintings, and later of numerous panels of Dutch, Flemish, and German painters were precisely placed in time and the cutting years of the respective oaks estimated.

A Problem Arises

The problem with art-historical dendrochronology arose when during the analysis of oak panels used by Rembrandt, Rubens and numerous other painters who worked between the 14th and the middle 17th century, a new tree-ring pattern appeared which did not cross-match with any of the then existing oak chronologies (3, 5, 11).

Since most of the tree-ring series of these panels matched each other extremely well, a floating chronology spanning 530 years was established, and this new tree-ring pattern, initially thought to be characteristic for the Netherlands, was called Netherlands Type II (3). Support for this assumption was the fact that panels of English paintings showed the same tree-ring pattern (7). Thus it was assumed that these oaks grew in a region along both sides of the Channel. That the timbers had been imported into the Netherlands seemed improbable since it would imply continuous trade connections from the 14th (paintings of the Cologne School) to the 17th century (paintings of Rembrandt), always bringing timbers from the same source.

It was striking, however, that no paintings from later than about 1650 had the Type II tree-ring pattern. Painters from around 1700 such as the Dutchman A. van der Werff (1659-1722) generally used panels datable with the South German reference chronology. If these latter artists used panels with the Netherlands Type II ring pattern, the timbers had been felled before 1650; the respective panels had either been stored for a few decades or were being re-used.

In Search of a Solution

In an attempt to tie down the Type II chronology, an independent tree-ring chronology was constructed using living oaks and successively older timbers from wind-mills and other buildings in the Netherlands. This resulted in a chronology extending back to 1036 A.D. (5) (Type I chronology). However the Type II tree-ring pattern still failed to crossdate with it. The position in time of the Type II chronology was assigned on the basis of some ring patterns which showed apparent similarities with both, Types I and II. The tentative nature of this weak cross-matching resulted in the Type II chronology being withheld from publication.



Fig. 1 Natural distribution of oak. *Quercus robur* L. (European oak) is distribution inside the heavy line, and *Quercus petraea* Liebl. (sessile oak) is found in the area to the west of the dashed line. The source of oak timbers of type II tree-ring pattern and the places of their utilization as panels are indicated by arrows.

In the meantime a number of new long oak chronologies have come into existence, so that from South Sweden through Central and Western Europe a dense grid of reference material is now available. In the light of this new material and with a better understanding of the level of similarity which can be expected between chronologies from distant localities, it appeared increasingly unlikely that the Type II tree-ring pattern was from the Netherlands. This idea gained support from the discovery that some art historical monuments in Lübeck with hundreds of oak boards, and altar pieces in Hamburg also contained the Type II tree-ring pattern. Therefore other provenances had to be taken into account.

## Results

### 1. Provenance Discovered, Timber Dated

Within the natural distribution of oak in Europe (Fig. 1) there are still several areas lacking long tree-ring chronologies. But Eastern Europe and especially the coastal range of the eastern Baltic Sea seemed to represent the most probable sources for oak timbers imported to the Netherlands. According to historical and archival evidence (4, 12, 13), the Vistula River (Weichsel) and its tributaries Bug, Narew and San, permitted access for logging to the large Polish forests. As this evidence was emerging, an independent investigation of the English art-historical chronologies (which matched with Netherlands Type II) suggested that the timber had derived from Eastern Europe, possibly Poland or Lithuania (1, 2). But it was acknowledged that positive dendrochronological proof was still missing.

In order finally to resolve this question, we undertook a study of building timbers from churches and other historical buildings, and from art historical objects and archaeological excavations in northern Poland around Gdansk. Thirty paintings of various unknown Gdansk painters from the 15th to the 17th century were analysed in the Museum Narodowe, Gdansk, and in the Museum of the Diocese, Gdansk-Oliwa. In addition more than 200 core samples were taken from different monuments in and around Gdansk. Several hundred core samples were also taken from living oak trees. The new chronology extended from A.D. 1000 to 1985 using more than 300 tree-ring series (6). The Type II chronology matches this Polish chronology with a highly significant Students 't' value and a high percentage of parallel variation and according to this dating spans the years 1115 to 1643. Thus it was shifted by six years towards the present from our original tentative placement. Paintings of known Gdansk artists such as Andrej Stech (1635-1697) (Fig. 2) and panels of unknown painters could now be dated between the 15th and the 17th century (Table 1).

Table 1. Dendrochronologically dated panels of Gdansk painters

Paintings	Artist	Latest heartwood ring	Dendrochronol. felling range sapwood allowance 13..15....19 +x
St.Elizabeth Shrine	Gdansk unknown ca.1410	1381 1370 1372 1375 1369 1370	1394..1396....1400 +x
St.Cathrine-baptistry-	Gdansk unknown dat.1589	1569 1562 1574 1570 1539	1587..1589....1593 +x
Fire in Gdansk	Milwitz,B. ca.1656	1585	1598..1600....1604 +x
Noah before the Flood	Gdansk unknown 17th c.	1418 1440	1453..1455....1459 +x
Self portrait	Stech, A. dat.1675	1637 1638	1651..1653....1657 +x



Fig. 2 Oak panel, self-portrait by A. Stech, Narodowe Museum, Gdansk, Poland.



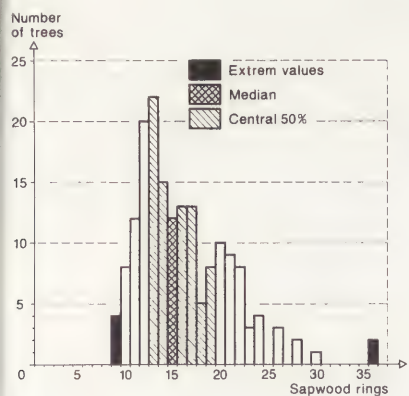


Fig. 3 Distribution of the number of sapwood rings in 179 oak trees from north Poland.

It is interesting to trace the occurrence of Type II timbers. They are found in paintings by Rembrandt in Leiden and Amsterdam, by Rubens in Antwerp, by van der Weyden in Brussels and by van Eyck in Bruges. They are present in some altars of unknown early German painters in Cologne, in some cases in the same altar alongside panels with the South German tree ring pattern, and in art-historical monuments in Lübeck and Hamburg, thus confirming the trade connections as shown in Fig. 1. Timbers with the Type II ring pattern have only once been found as building timbers; this was a rafter in Amsterdam which had been cut around 1615. This finding supports the view that most of the Baltic oak was exported in form of planks and boards. Type II timbers are never found after 1650 because the Thirty Years War cut the trade routes across the Baltic Sea. Finally the Second Swedish-Polish War from 1655 to 1660 caused the total breakdown of the Vistula trade.

## 2. Sapwood Allowance

With the discovery of the provenance for the oak panels with Type II ring-patterns and with correction of their dating to six years later, new evidence arose for the sapwood allowance (Fig. 3). An analysis of the number of sapwood rings from 179 oaks from northern Poland resulted in a median value of 15 rings with 50% of all values lying between 13 and 19 rings. Lower and upper extremes are 9 and 36 rings. Since there is an indication of a west-east gradient of decreasing sapwood rings, in every dating of art objects the provenance of the wood must be taken into account (10). It should be further emphasized that dendrochronology can yield an exact date for the last ring on the art object, but considerations about the cutting year of the tree are based on a statistical evaluation and can be no more than an estimate.

Table 2 shows the combined effect of the date correction of the Netherlands Type II chronology and of the adjustment of the sapwood estimates. The net result is a change in estimated date of only one year, so small as to be inconsequential to the art historian.

Table 2. Effects of dating correction of the Netherlands Type II chronology and improvement in the estimated number of sapwood rings on dendrochronological dating of panels of R. van der Weyden and his circle of painters

Paintings	Dendrochronological felling range of the oak trees	
	before dating correction with arithmetic mean sapwood allowance of $20 \pm \frac{5}{2}$ yr	after dating correction with median sapwood allowance of 13..15....19+x yr
St. Luke painting the Virgin (Boston)	$1424 \pm \frac{5}{2}$	1423..1425....1429 +x
Woman with headdress (Berlin)	$1425 \pm \frac{5}{2}$	1424..1426....1430 +x
Miraflores Altarpiece (Berlin)	$1426 \pm \frac{5}{2}$	1425..1427....1431 +x
Bladelin Altarpiece (Berlin)	$1434 \pm \frac{5}{2}$	1433..1435....1439 +x
Columba Altarpiece (Munich)	$1439 \pm \frac{5}{2}$	1438..1440....1444 +x
St. John Altarpiece (Berlin)	$1443 \pm \frac{5}{2}$	1442..1444....1448 +x
Portrait of a Lady (Washington)	$1452 \pm \frac{5}{2}$	1451..1453....1457 +x
Crucifixion (Philadelphia)	$1452 \pm \frac{5}{2}$	1452..1454....1458 +x
St. Luke painting the Virgin (Munich)	$1473 \pm 5$	1472..1474....1478 +x
St. John Altarpiece	$1498 \pm 5$	1497..1499....1503 +x

### Conclusion

The re-dating and re-interpretation of the Netherlands Type II chronology does not affect other art-historical dating determinations. Thus dates previously established for oak panels, sculptures and furniture with ring patterns of Dutch, French or West German trees are unaffected, as are dates for beech panels with paintings by artists such as Lucas Cranach, and for stringed instruments made of spruce wood. In short, one aspect of art-historical dendrochronology was thrown into doubt, and the resulting studies have led to a successful resolution of the problem, with interesting implications for the study of medieval trade patterns. Confidence in art-historical dendrochronology is sustained.

### References

- 1 Baillie, M.G.L.; J. Arch. Sci. 11, 371-393 (1984)
- 2 Baillie, M.G.L., Hillam, J., Briffa, K.R. & Brown, D.M.; Nature 135, 317-319 (1985)
- 3 Bauch, J.; BAR (International Series) 51, 133-137 and 307314 (1978).
- 4 Dollinger, O.; Die Hanse. A.Kröner Verlag, Stuttgart (1966).
- 5 Eckstein, D., Brongers, J.A. & Bauch, J.; Tree-Ring Bull.35, 1-13 (1975).
- 6 Eckstein, D., Wazny, T., Bauch, J. & Klein, P.; Nature 320, 465-466 (1986).
- 7 Fletcher, J.M.; J. Arch. Sci. 4, 335-352 (1977).
- 8 Hollstein, E.; Mitteleuropäische Eichenchronologie. Zabern Verlag, Mainz (1980).
- 9 Huber, B. & Giertz, V. ; Conf. Rep. Austrian Acad. Sci. 178, 32-42 (1969)
- 10 Hughes, M.K., Nilson, S.K. & Legett, P.A.; J. Arch. Sci.8, 381-390 (1981).
- 11 Klein, P.; Dendrochronologia 3, 25-44 (1986).
- 12 Krannhals, D.; Danzig und der Weichselhandel in seiner Blütezeit vom 16. zum 17. Jh., Leipzig (1942).
- 13 Rath, R.E.; Der Weichselhandel im 16. Jh., Marburg (1927).



## SUMMARY

One of the main tasks of the technological study of paintings is to determine the structure of the paint layer and fine-crystalline pigments. But in many cases any taking of the paint sample suitable for work according to standard procedures of X-ray structural or microscopic analysis is either undesirable or impossible.

In the present paper a working variant of a camera, focused directly from the X-ray tube target, is suggested. The camera has a diameter of 61mm and permits getting X-radiographs of paints from the painting surfaces or movements from an area of 16 mm<sup>2</sup> or less. The painting surface under study is pressed to the corresponding section of the camera focal circumference. An exposure time with an electric power on the tube 100W is 0.3-1.5 hour on a 30R sensitive film. The diffraction angles practically measured are 35-105°. The width of the diffraction lines on the film does not exceed 1mm.

## THE FOCUSING CAMERA FOR NON-DESTRUCTIVE X-RAY DIFFRACTION ANALYSIS OF PAINTING SURFACE

Dr. Kossolapov A.J.  
The Head of Lab.Sci.Exam. Works of Art  
The State Hermitage Museum  
191065 Dvortsovaya nab.34, Leningrad, USSR

Introduction

One of the main tasks of the technological study of paintings is to determine the composition and structure of the painting materials, in particular, the painting layer pigments. Currently, the most suitable procedure used for determining the composition may be considered the non-destructive X-ray fluorescence analysis of the painting surface (the first versions of such devices were likely introduced by Ch.Lahanier, The Sci.Lab. Museums of France) and the emission spectral microanalysis with a laser sample taking, so-called laser microprobe used by the author in the Hermitage since 1974. The latter method is particularly good when it is necessary to determine trace elements usually identified in emission spectral analysis in concentration not lower than 0.001-0.01%.

Many fine-crystalline pigments, having spectroscopically the same or rather similar chemical composition can, however, be of different structure and, therefore, represent quite different substances. For example, among blue pigments on copper base there are natural and artificial azurite, basic verdigris, copper phthalocyanine, copper indigo, among green pigments, besides malachite, use was made of chrysocolla, a neutral verdigris, Scheele green, Schweinfurth green.

To identify the structure of pigments, the samples selected are studied with the help of a polarisation microscope or the X-ray diffraction analysis (XRDA). The former requires a good and rather big (several  $\mu\text{m}$ ) monocrystal of the pigment which would enable to state both the refraction index and the type (uniaxial, biaxial, amorphous) by using conoscopic figures. It is not always possible to select a suitable monocrystal from the painting even when it is relatively easy to take a sample.

With the help of a diffractometer or Deby camera the XRDA of a sample taken usually gives diffraction lines of hydrocerussite (white lead) which, as a rule, forms a part of paints, and sometimes it gives diffraction lines of the pigment being determined, if it is present in the mixture in a sufficient amount. The latter condition is observed rather seldom and that is why for the technological study of paintings the XRDA is used mainly to identify the ground where it is important to distinguish anhydrite from gypsum, chalk, and also to determine the main components of colored grounds -whiting, ochre, bole etc.

Thus, the main drawback of XRDA in analysing painting pigments is its destructive character and limited sensitivity to be accounted for by the small size of a sample taken. It is because of this that the method proves hardly applicable which deprives museum laboratories of a number of useful possibilities.

Nevertheless, the idea to use for XRDA a camera in which the sample studied represents a sufficiently big fragment of the painting surface itself, and the focusing of the diffraction lines is accomplished by corresponding geometry, -the idea was found to be very useful helping to eliminate the main defects of the method mentioned above.

Design of apparatus

In the Laboratory of Scientific Examination of Works of Art of the Hermitage museum there was built in 1986 a working variant of a focusing X-ray camera (Fig.1). The camera is a hollow semicylinder 25mm in height and inner diameter 161mm (pos.1), fixed on moving bars (pos.2) on the casing of sharp-focus X-ray tube (USSR made model BSV-7), (pos.6). The size of the tube target (pos.7) is 2000x200  $\mu\text{m}$ , the radiation selection angle is about 5°. This gives a working projection of the target in the direction of the radiation propagation of approximately 200x200  $\mu\text{m}$ . The angle between the direction of the tube radiation and the normal to the painting surface pressed to the camera section is  $\beta=60^\circ$ , the value of the target projection on the focal circumference being  $200/\cos 60^\circ=400 \mu\text{m}=0.4\text{mm}$ . The diffraction lines are photographed on a film closely pressed to the inner (focal) surface of the semicylinder (pos.3). The collimator (pos.5) limits the size of the radiation spot to the width of 8.0mm on the painting surface in the focusing plane and up to 2.0mm in height, correspondingly perpendicular to the focusing plane. The size of the fragment of the painting being analysed is thus  $8.0 \times 2.0=16\text{mm}^2$ .

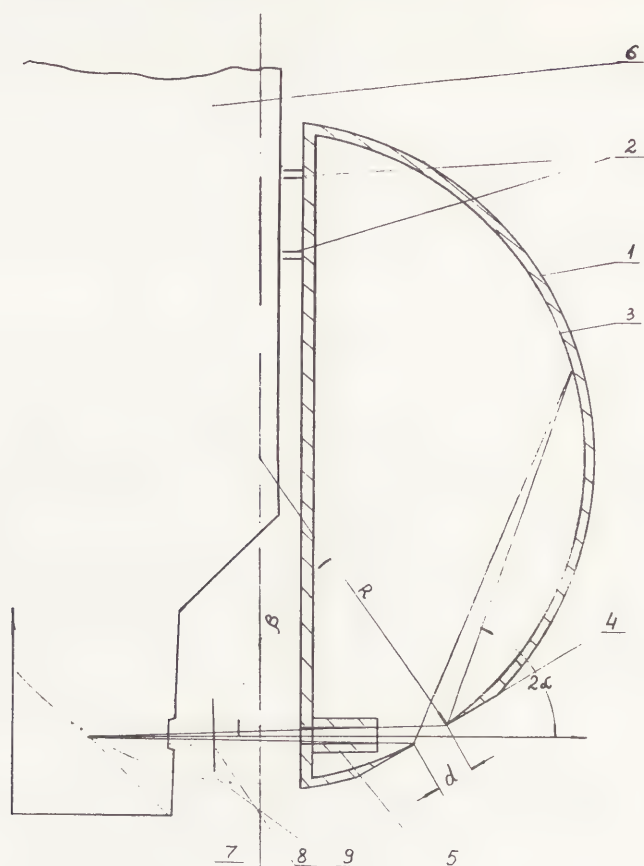


Fig.1 The focusing X-ray camera mounted on the tube.  
1-camera, 2-moving bars, 3-focal circumference to which X-ray film is pressed, 4-the plane to which an analysed surface is pressed, 5-collimator, 6-sharp-focus X-ray tube in its casing, 7-focus(target) of the tube, 8-selective filter, 9-Be-window of the tube.

#### Diffraction lines width

As shown by a rather bulky calculation, the greatest contribution to the broadening of diffraction lines (disfocusing) is given by the deviation of the painting surface from the focal circumference. The value of this broadening  $\mathcal{Z}_1$  is equal correspondingly

$$\mathcal{Z}_1 = \frac{d^2}{8R} (\operatorname{tg} \theta - \operatorname{tg}(\theta + 2\alpha)) \quad (1)$$

where  $R$  (mm) being the focal circumference radius,  $d$  (mm)-the length of the chord of the focal circumference section,  $2\alpha$  - the angle between the direction of the initial and the diffracted radiation beams,  $\theta$  - the angle between the direction of the initial radiation beam and the painting plane. In this camera we have  $2R=161\text{mm}$ ,  $d=8.0\text{mm}$ ,  $\theta=60^\circ$ .

The value  $d^2/8R$  in the expression (1) is the greatest deviation of the painting plane from the focal circumference; the value of the angular factor  $(\operatorname{tg} \theta - \operatorname{tg}(\theta + 2\alpha))=f$  depending on the diffraction angle  $2\alpha$  is given in Table 1.

Table 1. The angular disfocusing factor  $f$  and the calculated width of diffraction line, (mm)

Diffraction angle, degrees	35	40	50	60	70	80	90	100	105
Angular disfocusing factor, $f$	13.2	7.4	4.5	3.5	2.9	2.6	2.3	2.1	2.0
Full width of the diffr. line $\mathcal{Z}$ , mm	1.72	1.14	0.85	0.75	0.69	0.66	0.63	0.61	0.60

The full value of disfocusing (the diffraction line width), besides the  $\mathcal{Z}_1$  contribution, is to be accounted for also by the final value of the target projection on the focal circumference (0.4mm). The values of the full disfocusing  $\mathcal{Z}$  are also given in Table 1. Theoretically, the size of the analysed painting fragment in the direction perpendicular to focusing plane, gives in line centre a



broadening of the 2nd order of smallness. Practically, it is advised to take the size of 1.0-2.0mm (in the camera described 2.0mm). Then, with a camera 25mm in height, the defocusing on the edges of lines registered on the film pressed to the focal circumference is not very noticeable.

The data given show that the suggested variant of X-ray camera permits the diffraction pattern to be reliably registered from the fragment of the painting surface of the size 8.0 x 2.0mm in the range of diffraction angles ( $2\theta$ )  $35^\circ$ - $105^\circ$ . In this case, for angles  $40^\circ$  and more the width of lines does not exceed 1.0mm.

#### Some details of practical use

The exposition time when the tube electric power is 100W, using a selective filter which decreases the ratio of the intensities  $K_\beta$  and  $K_\alpha$ -lines of the copper anode up to 1/300 and photographing on X-ray film with 30 reverse roentgens sensitivity, is 0.3-1.5 hour depending on the dispersive properties of the material studied.

The determination of the diffraction angles with the registered lines may be done with the help of a special pattern or by measuring the distances of every line from the film edge with account taken of the calculated value of the camera dispersion which is 0.357 degr./mm. Practically, however, it is more convenient to prepare beforehand a set of diffraction standards of different painting pigments with the help of the same camera. Then, the identification of the pigment can be easily carried out without any measuring by way of visual comparison of the films.

When working with the focusing camera, it should be taken into consideration that qualitatively, visual comparison of the blackening of the lines lying on different diffraction angles may not correspond to the lines intensities ratio given in reference literature for a given substance because there is a dependence of the line broadening on the diffraction angle. Thus, for example, the lines having in the reference book equal intensities and being photographed in the camera above described in the diffraction angles  $40^\circ$  and  $105^\circ$  correspondingly will appear different in blackness, as the broadening of lines at  $40^\circ$  is about 3 times more than at  $105^\circ$  (see Table 1). Of course, the integral intensity of such lines measured on a microphotometer will be the same.

In addition it should be said that the camera may be used not only for paintings but also for any museum monuments if their corresponding surfaces can be pressed to the focal plane section.

In perspective it seems expedient to make a universal device which would combine the possibilities of X-ray fluorescent analysis (on a SCD detector of high resolution) and X-ray diffraction analysis of the painting surface.





## SUMMARY

In recent years it has been observed that some oil paintings on canvas in Japan have developed crystal growths within the structure of the paint film as well as on the surface. Crystals from four paintings were analyzed by conventional micro-chemical tests, X-ray fluorescence spectroscopy and X-ray powder diffraction, and finally by experimenting with a newly designed non-destructive X-ray diffraction instrument. The crystals were identified as some form of zinc sulfate hydrate probably formed by the transformation of zinc oxide in the ground or paint layers.

## A PRELIMINARY REPORT ON THE EXAMINATION OF CRYSTALS FOUND ON OIL PAINTINGS IN JAPAN USING NON-DESTRUCTIVE X-RAY DIFFRACTION

Masako Koyano  
Art Conservation Laboratory  
4-27-4 Honcho, Nakano-ku, Tokyo 164, Japan  
Takeo Kadokura  
Tokyo National Research Institute of Cultural Properties  
13-27 Ueno Park, Taito-ku, Tokyo 110, Japan

## Introduction

The technique of oil painting was introduced into Japan about 100 years ago. Since then oil painting has become very popular among painters and collectors, increasing the number of paintings in Japan. Until recently the paintings have not been protected in storage and exhibition from the effects of Japan's predominately humid climate\*.

Recently conservators in Japan report that unusual crystals are found to have grown on many oil paintings. In fact, in the past, crystal growths have been observed on traditional Japanese paintings on silk, but the crystals have never been investigated. These crystals are visually disfiguring and often destroy the paint film in the process of their growth. It is because of this that we are now in full pursuit of the origin and mechanism of this crystal growth.

The attitude of the Japanese government is very strict about not taking samples from cultural properties and most collections follow this rule. In this case, special permission was obtained from owners to take small discreet samples of pigment, ground and crystals from the paintings examined. However, when the Tokyo National Research Institute for cultural Properties developed a special apparatus for non-destructive X-ray diffraction analysis in 1984, this crystal growth problem provided an opportunity to experiment with the capabilities of this fast, accurate equipment.

\*Temperature 27°C, humidity 77% in average in Tokyo, in August.

## Examination and Analysis

Between 1971 and 1986, four modern oil paintings on canvas were examined at the Art Conservation Laboratory in Tokyo, and were found to have a crystal growth causing obscuration and disruption of the paint layers (See summary in Fig.1). Samples of the crystals from each painting were collected with a fine brush and were analyzed by five different outside laboratories by various destructive techniques. In the latter three paintings it was possible to obtain samples of the pigments involving the crystals. Ground samples were taken from all four paintings. The samples were taken from discrete areas of the paintings using a scalpel under binocular microscope. In 1986, for the fourth painting, more extensive analysis was undertaken at the Tokyo National Research Institute of Cultural Properties using direct non-destructive readings from the painting with a specially designed X-ray diffraction apparatus that will be described in the following section.

Landscape by Zenzaburo Kojima, 1943, 45.5x53 cm (Fig.2), was examined in 1971, and had crystals within the structure of the paint film as well as on the surface. Those on the surface appeared somewhat sugary under the microscope. Large transparent to whitish crystals about 2mm long were observed within the paint layers and appeared to have broken through the paint layer in the process of their growth, causing crater-like ruptures and loss of paint (Fig.3).

The crystals were water soluble\* and seemed attracted to moisture. They were observed to change into liquid when the weather was hot and humid and when brought into an air conditioned room crystals were formed again at once. The crystals were insoluble in resinous solvents.

\*Other crystal examples have been found which are not water soluble.

The ground of this painting was identified by micro-chemical tests\* as zinc oxide. The pigments were not sampled or identified. The crystals were analyzed by Professor Hachiro Oguchi of Tokyo University of Arts using X-ray fluorescence spectroscopy, and X-ray powder diffraction, and were identified as zinc sulfate.

\*See "Technical Studies in the Field of the Fine Arts, Vol.IV" (ed. by W. M. Freitag, 1975, Garland Publishing, Inc., New York and London) page 222.

TITLE,ARTIST	CRYSTAL OBSERVATION	CRYSTAL,GROUND,PAINT	DATE	LAB	METHOD
Landscape (1943) by Z. Kojima	Fine sugary allover	Crystal: Zn sulfate Ground: Zn oxide Colors: not exam'd	1971 1971	TUA ACL	XRF CM
Dolls (1947) by S. Suzuki	Large rupturing paint film in blue, green and white	Crystal: Zn sulfate Ground: Zn, Pb, Ti Colors: Prussian blue (Ferric ferrocyanide) Viridian (Hydrated Cr oxide) Zn oxide	1981 1981 1981 1981 1981	McC McC McC McC McC	EM-XRF EM-XRF EM-XRF EM-XRF EM-XRF
Still Life with Urn (1933) by A. Hirooka	Crust allover	Crystal: Zn sulfate hydrate Ground: Zn oxide Colors: Vermilion (Mercuric sulfide)	1984 1983 1984	LACMA ACL LACMA	XRD,CM CM XRF
Still Life with Lemons (1930's) by T. Kobayashi	Fine sugary on fruit, blue spots on reverse of canvas	Crystal: Zn sulfate heptahydrate Ammonium Zn sulfate hydrate Ground: Pb carbonate  Colors: Co aluminate Vermilion (Mercuric sulfide) Zn oxide Cd yellow lemon	1986 1986 1986 1986 1986 1986 1986	NGAL TNRI TNRI ACL TNRI TNRI TNRI	XRD,LM CM XRD.sp XRD.sp CM XRD.sp XRD.sp XRD.sp XRD.sp
Labs: ACL = Art Conservation Laboratory TUA = Tokyo University of Arts McC = Walter McCrone Associates LACMA = Los Angeles County Museum of Art NGAL = National Gallery of Art, London TNRI = Tokyo National Research Institute of Cultural Properties					
Methods: EM = Electron microprobe CM = Chemical microscopy XRD = X-Ray diffraction XRF = X-Ray fluorescence LM = Laser microprobe					

Fig.1 SUMMARY OF PAINTINGS EXAMINED

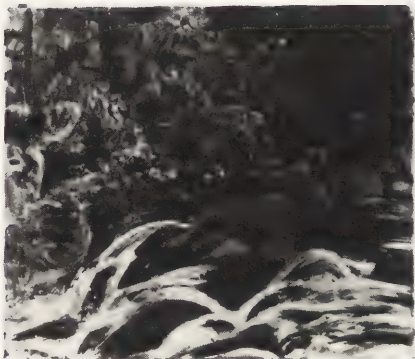


Fig.2: 'Landscape' by Z. Kojima



Fig.3: Fine sugary crystal on the 'Landscape' of Fig.2 (x45)





Fig.4: 'Dolls' by S. Suzuki



Fig.5: Transparent crystal in the large rupture of the paint film of Fig.4 (x40)

Dolls by Shintaro Suzuki, 1947, 60.2x45 cm (Fig.4), examined ten years later in 1981, had severe ruptures of the paint film primarily in the green, blue and white of the dolls' skirts (Fig.5). Pigment, ground and crystal samples were sent to Walter C. McCrone Associates, Inc., in Chicago, Illinois, U.S.A., for analysis by electron microprobe, X-ray fluorescence spectroscopy. The ground was found to contain zinc, lead, titanium, barium and sulfur. The green was found to contain mainly chromium, most likely viridian, hydrated chromium oxide  $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ . The blue produced high iron readings, probably Prussian blue, ferric ferro-cyanide  $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ . The crystals contained zinc, sulfur and oxygen probably zinc sulfate.

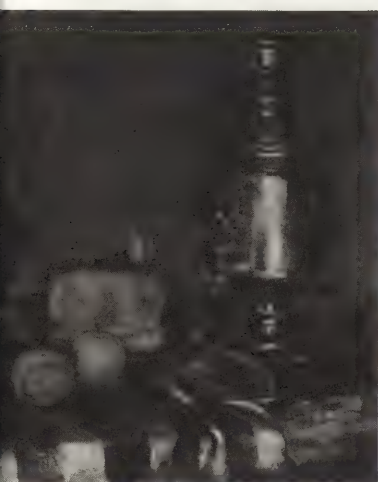


Fig.6: 'Still Life with Coffee Urn' by A. Hirooka

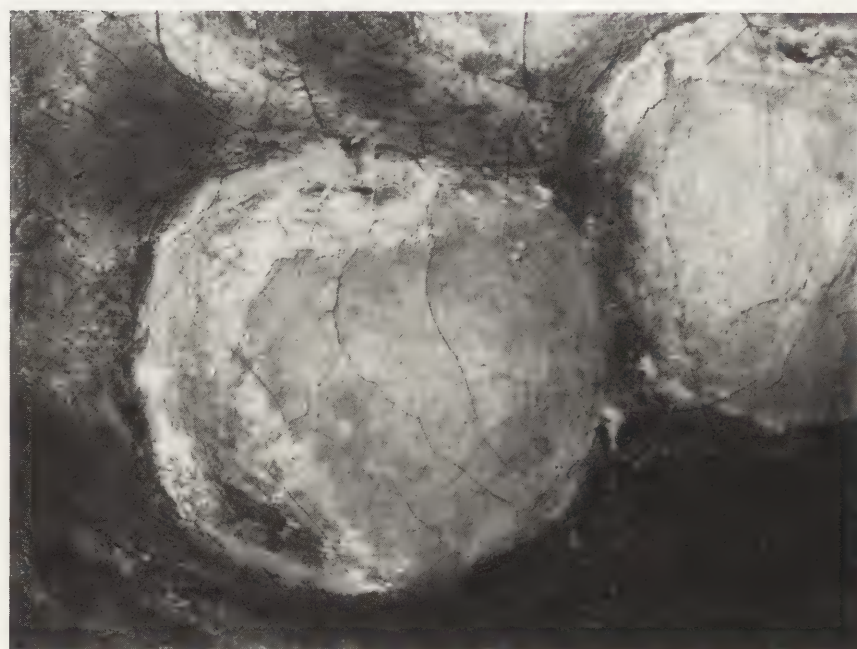


Fig.7: Crust of fine crystals on the paint film of Fig.6 (x45)



Still Life with Coffee Urn by A. Hirooka, ca. 1933, 72.4x60.7 cm (Fig.6), examined in 1983-84, had a crust of fine crystals over the entire surface (Fig.7). Under ultraviolet light the crystal coating fluoresced yellow like a varnish coating. The ground was identified by micro-chemical tests as zinc oxide. Pigment samples were sent to Mr. James Druzik then at the Los Angeles County Museum of Art, Los Angeles, California, U.S.A., for examination by X-ray fluorescence spectroscopy and powder X-ray diffraction. The red contained mercuric sulfide and lead oxide. The brown contained iron, zinc and lead. The crystals were identified as zinc sulfate hydrate (JCPDS No. 33-1476).

Still Life with Lemons by Tokusaburo Kobayashi, ca. 1930, 45.5x53 cm (Fig.8) was examined in the spring of 1986. Most of the fruit and the bowl had a fine crystal crust on the surface (Fig.9). In addition, the reverse of the canvas had scattered spots that looked as if the canvas were wet (Fig.10). Through Mr. Garry Thomson of the National Gallery of Art, London, England, a crystal sample was analyzed by a combination of X-ray powder diffraction and laser microprobe, and identified as zinc sulfate heptahydrate  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (JCPDS No. 9-395). This painting was again analyzed at the Tokyo National Research Institute using non-destructive direct reading X-ray diffraction. The ground was identified as lead carbonate hydroxide (JCPDS No. 13-132). The red of the oranges was found to be vermilion mercuric sulfide  $\text{HgS}$ . The blue was cobalt aluminate  $\text{CoO} \cdot \text{Al}_2\text{O}_3$ . The white was zinc oxide. The crystals were found to be ammonium zinc sulfate hydrate  $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (JCPDS No. 35-767) (Fig.11). The number of water molecules, 6 or 7, depends on the level of humidity. This identification was verified by sample in conventional X-ray powder diffraction. To confirm the presence of ammonia, the crystal was examined by ion chromatography, and ammonium ion was detected (Fig.12).

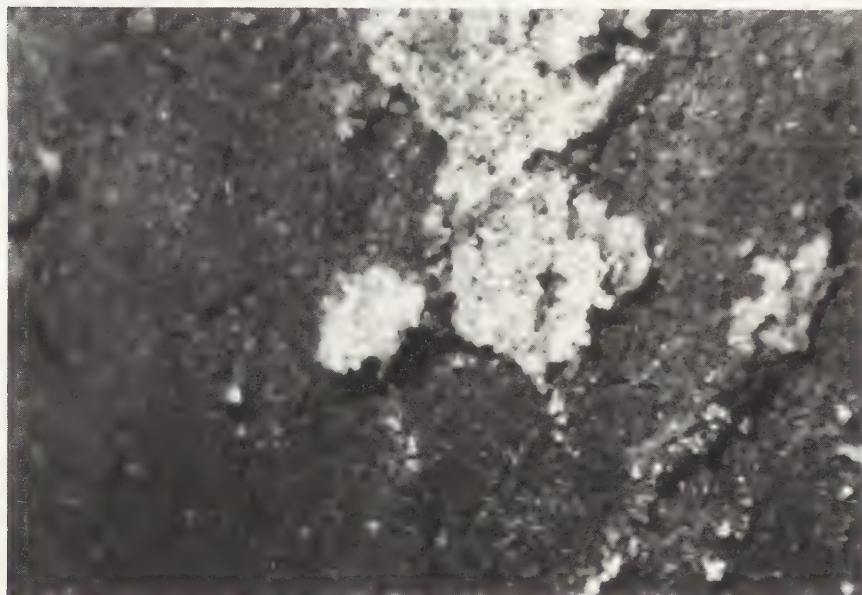


Fig.9: Fine crystal crust on the painting, Fig.8 (x45)



Fig.8: 'Still Life with Lemons' by T. Kobayashi

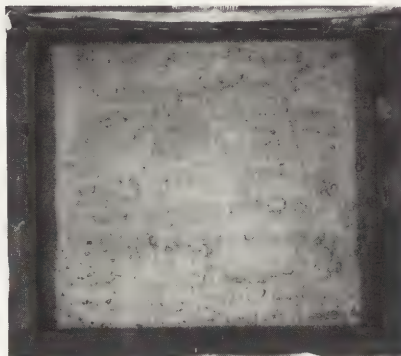


Fig.10: Spots on the reverse of painting of Fig.8



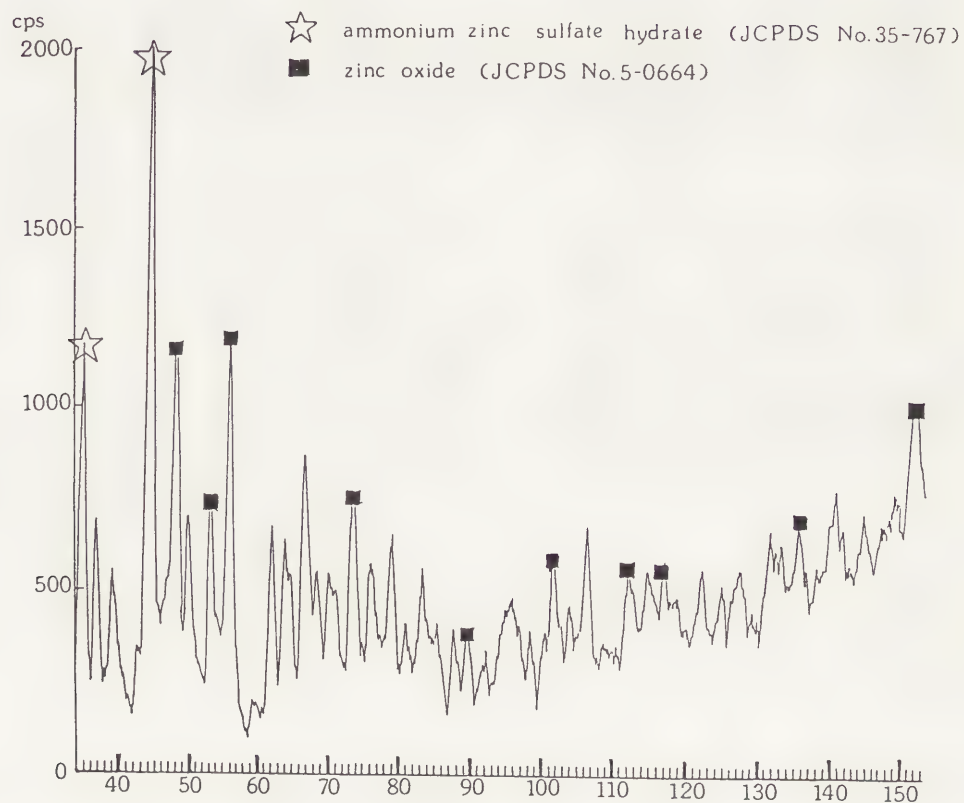


Fig. 11: Chart taken by specially designed X-ray diffraction apparatus

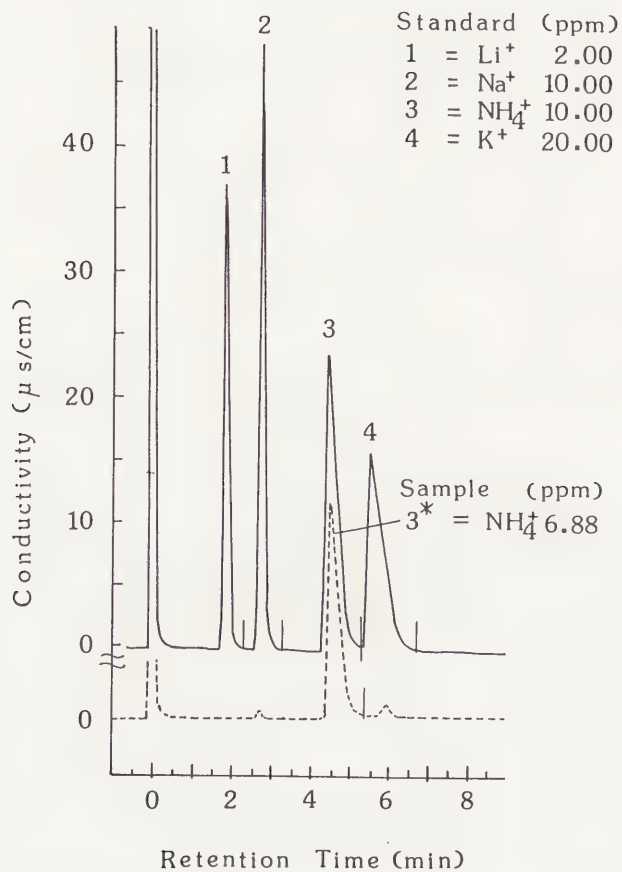


Fig. 12: Chromatogram of the standard and sample

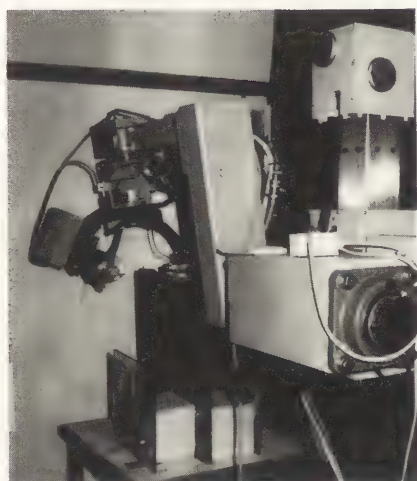


Fig.13:X-Ray diffraction apparatus specially designed by Tokyo National Research Institute

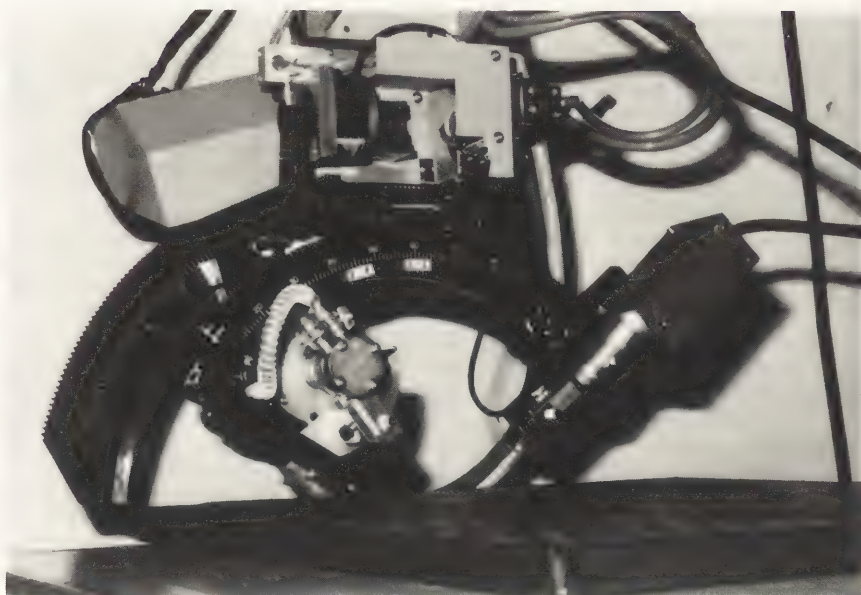


Fig.14: Detail of Fig.13.

#### Non-Destructive X-Ray Diffraction

This apparatus was custom designed for the Tokyo National Research Institute in 1984, to use in temple sites to analyse wall and ceiling paintings (Fig.13). It is a unique portable machine separate from the control panel with a mobile arm to allow aiming the goniometer in many directions (Fig.14).

It has the advantage of being able to read directly off the surface of an object, identifying individual compounds and producing results in 20 minutes. It has two disadvantages. First, that the beam is perhaps one third the strength of conventional powder diffraction due to the open nature of the apparatus, and thus a larger sample is required, a minimum of 5 mm<sup>2</sup>. Reading of an irregular surface further reduces the sensitivity of the reading. For the painting analysis, if necessary, a lead mask can be used over the object with a 0.7x1.0 cm rectangular opening to expose the desired sample area. The second disadvantage is that in order that the goniometer does not touch the object, the angle of incidence must be limited to at least 15° ( $2\theta = 30^\circ$ ), and thus the full range of diffraction is not scanned. A chromium target ( $K\alpha_1 = 2.2896 \text{ \AA}$ ) is used for the above angle of incidence and it cannot measure internal crystal space larger than  $d = 4.423 \text{ \AA}$ . In such a case, the sample pattern must be compared to that of a known compound or to JCPDS reference cards. Of course, this type of analysis is limited to shallow surface readings and does not address organic components. The beam has a maximum radius of about one meter. During operation that area around the machine should remain clear or lead shielding be used.

#### Conclusions

The crystals in the four cases described were consistently identified by various means of analysis as zinc sulfate hydrate, probably containing ammonia. It appears to be formed from sulfate ions present in the ground and/or paint, in high humidity, in the presence of ammonia. Air pollutants and decomposing materials from the painting sizing or medium may furnish these components. The high temperature and humidity of Japan's weather, especially summer, are considered to be an important factor responsible for accelerating the growth of the crystals. Further research needs to be done to investigate the mechanism of transformation of zinc sources in the painting and sources of ammonia and other contributing materials. Certainly the non-destructive method of X-ray diffraction analysis offers great potential for studying this kind of problem on a larger scale.



## BIBLIOGRAPHY

1. G. Thomson, *The Museum Environment* (London: Butterworths, 1978) p.110.

Resume: Zinc sulfate takes into its crystal structure a certain number of molecules of water. These become part of the crystal structure and cease entirely to be liquid water. Some of them are loosely bound and will leave the crystal in conditions of low R.H. forming water vapor, to condense again into the crystal structure if the R.H. rises above a certain level.

2. K. Hirota and S. Nobuoka, "A Study of Deterioration of White Colorant in Painting" *Shikizai-Kyokai-Shi*, 55, No. 9 (1982): pp. 623-629.

Resume: With the purpose of elucidating the cause of cracks and deterioration in the final paint film of an overlapped oil painting, a relation between changes with time in paint film and the overlapped paint film has been investigated by coating an oil paint composed primarily of white lead, zinc white, and titanium white on a canvas and then analyzing products formed in the paint film during a period of time. As a result, the following new facts were observed:

1. With regard to a known knowledge that lead white and zinc white as active pigments react with vehicle to form metal soaps, the experimental results could not afford a persuasive explanation for their quantitative relations. However, it was observed that they were different as to the amounts of metal soaps formed.
2. As for the zinc white paint film, it was inferred that zinc soap was remarkably formed and the formation of the zinc soap was the major cause of cracks in the final paint film.
3. In contrast with a well-known knowledge that pigments tending to react with vehicle to form metal soaps are less chalked, the experiments conducted this time revealed that chalking was accelerated as metal soaps were formed, but that no formation of metal soap was observed and also no chalking was recognized for the paint film of titanium white as inert pigment.

3. R. J. Gettens and G. L. Stout, *Painting Materials* (New York, Dover Publications, 1966) p.176.

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## RESUME

Les changements de composition du blanc de plomb au cours du temps, dus au mode de préparation du pigment d'une part, et à l'origine du minéral d'autre part, sont exploités grâce à deux techniques non destructives en vue de la datation et de l'authentification de peintures de chevalet.

L'analyse des impuretés du blanc de plomb par microsonde nucléaire a permis de mesurer les teneurs en Cu et en Ag d'oeuvres du 15e au 20e siècle. Cependant, les limites de détection de l'appareil devront être reculées pour élargir l'utilisation de la méthode.

La mesure de variation isotopique  $^{206}\text{Pb}/^{204}\text{Pb}$  par spectrométrie de masse de peintures du 15e au 20e siècle a permis d'affirmer qu'un même réservoir européen a été utilisé du 15e au 18e siècle, tandis que des mines de plomb plus lointaines ont été progressivement utilisées à partir du 19e siècle pour la fabrication du pigment.

# ANALYSES DE PIGMENTS BLANCS APPLIQUEES A L'ETUDE CHRONOLOGIQUE DES PEINTURES DE CHEVALET - I BLANC DE PLOMB

J R Lancelot et A Allegret  
Laboratoire de Géochimie Isotopique,  
UP361 du CNRS  
Université de Montpellier II  
34000 Montpellier

B Nens  
Centre d'Etudes Nucléaires  
de Saclay  
Section d'étude et d'analyse  
isotopique et nucléaire  
91191 Gif-sur-Yvette

Ch Lahanier, J Rens, JP Rioux  
Laboratoire de Recherche des  
Musées de France  
Palais du Louvre  
75041 Paris

## INTRODUCTION

Le blanc de plomb, est utilisé depuis plus de vingt siècles dans la polychromie. Ses variantes physicochimiques et industrielles offrent un terrain de choix à l'application de méthodes nouvelles d'analyse et de microanalyse, adaptées à l'étude de prélèvements souvent hétérogènes et, dans le cas des peintures, nécessairement très petits.

L'objectif de la recherche est de dégager et d'affiner des critères d'identification et/ou d'authentification applicables à l'histoire de l'art, sur une tranche chronologique qui inclut l'histoire de la polychromie dans sa quasi totalité et toute celle de la peinture de chevalet.

Le blanc de plomb est l'un des pigments blancs le plus employé jusqu'au 19ème siècle. Sa toxicité lui fait préférer le blanc de zinc à partir de 1834 puis, au 20ème siècle, le blanc de titane.

Bien que le carbonate de plomb existe à l'état naturel sous forme d'hydrocérusite, le blanc de plomb est fabriqué depuis l'antiquité par attaque du métal au moyen de vapeurs d'acide acétique issues de vinaigre contenu dans des pots d'argile chauffés par du fumier. Les émanations, mélangées au gaz carbonique du fumier, transforment peu à peu l'acétate en carbonate. Le produit, gratté, est lavé, séché, tamisé puis mélangé à un liant.

Au 17ème et 18ème siècles, le blanc de plomb est surtout fabriqué en Angleterre et en Hollande à partir de minerais de Cornouaille, du Derbyshire et du Yorkshire etc..., selon le procédé de fermentation. La révolution industrielle du 19ème siècle, en développant les échanges commerciaux avec l'Amérique du Nord et l'Australie, introduit en Europe du plomb de composition différente. Dans la seconde moitié du 19ème siècle, les industries allemandes et autrichiennes dominent la fabrication de ce pigment. La production américaine s'affirme à son tour, au niveau international, à la fin du 19ème siècle. (1)

## Changements de composition du blanc de plomb, en Europe, du moyen âge au 20ème siècle

Les recherches publiées font apparaître trois modes de classement physico-chimique :

- la variation des teneurs en impureté (éléments mineurs et traces);
- la variation des rapports isotopiques du plomb;
- la modification de la composition cristalline;

Composition cristalline et niveaux d'impuretés majeures sont caractéristiques de la méthode de préparation; rapports isotopiques et impuretés en traces sont liés à l'origine du minéral.

### Analyse des impuretés du blanc de plomb par microsonde nucléaire

Houtman et Turkstra (1964)<sup>(2)</sup> Kühn (1966)<sup>(3)</sup> et Steinnes (1976)<sup>(4)</sup> ont opéré par activation neutronique sur 72 micro-échantillons (100  $\mu$ g) de blanc de plomb ainsi que sur 20 échantillons de fabrique; Kossolapov et Sizov (1984), par émission UV-visible avec source laser sur la surface de la coupe transversale (impact de 50 à 100  $\mu$ m).

Les résultats obtenus par activation neutronique font apparaître (par élément chimique) des différences importantes de teneur entre peintures d'une même école (hollandaise). Ces différences pour chaque élément chimique étudié sont attribuables à la préparation du prélèvement ou au mode expérimental. Considérées séparément, ces recherches montrent cependant quatre changements nets de composition :

- 1630 diminution des teneurs en chrome
- 1820 diminution des teneurs en argent, cuivre, manganèse et mercure (plomb purifié par extraction de l'argent - méthode de coupellation - puis en Angleterre par le procédé Pattison).
- 1850 augmentation des teneurs en zinc (extraction de l'argent par le procédé Parkes en Angleterre),
- 1961 diminution des teneurs en antimoine

dans la peinture hollandaise (16ème et 17ème), teneur plus élevée en argent et antimoine, et plus faible en cuivre et manganèse que chez les vénitiens (Titien, Tintoret et Tiepolo) du 16ème au 18ème.

Pour Kossolapov et Sizov<sup>(5)</sup>, le plomb brut contient de 0,1 à 1% d'argent et de 1 à 5% de cuivre que l'on retrouve dans le blanc de plomb: 500 à 1000 ppm d'argent et 0,1 à 1% de cuivre avant mise en oeuvre des procédés Pattison et Parkes. Les résultats d'analyse par activation neutronique seraient donc erronés d'un ou deux ordres de grandeur. Ces informations contradictoires sur le plan des teneurs, méritaient d'être vérifiées et complétées expérimentalement.

La microsonde nucléaire de Bruyère Le Chatel (CEA), équipée d'analyse non destructive de surface, permettant d'opérer sur des plages de 10 microns carrés, répond à la structure complexe de l'échantillon. Le balayage du faisceau de protons donne, en outre, la cartographie chimique de l'échantillon, les couleurs du moniteur étant liées à 16 niveaux de concentration. Cette expérience menée en 1984 révèle le degré d'homogénéité de la couche de blanc de plomb (éventuel mélange) et permet de localiser une zone non polluée pour effectuer le dosage quantitatif (5 et 6). Enfin, les limites de détection en mode PIXE (émission de rayons X induits par un faisceau de protons accélérés) sont expérimentalement proches du ppm dans un échantillon de faible épaisseur constitué principalement d'éléments de numéro atomique inférieur à 20, ce qui laissait escompter le dosage quantitatif des impuretés du blanc de plomb.

La détermination des limites de détection dans le blanc de plomb a nécessité d'effectuer la synthèse de standard d'acétate de plomb à 1% puis dilués à 0,1 et 0,01% contenant les éléments suivants : Ca, Ti, Cr, Fe, Cu, Zn, Mo, Ag, Sn, Ba. Trois gammes de standards ont été élaborés afin d'éviter des interférences spectrales. Ils ont été analysés avec des protons incidents d'énergie égale à 1,8 et 3 MeV donnant les meilleurs rapports pic/fond. Des 3 filtres d'aluminium d'épaisseur 10, 17 et 25  $\mu$ m placés devant le détecteur Si(Li), celui de 17  $\mu$ m s'est révélé le plus efficace pour atténuer l'émission X des éléments traces détectés entre 3 et 9 KeV, et au delà de 16 KeV.

Ces mesures ont permis de constater que les limites de détection à 1,8 MeV sont sensiblement les mêmes avec un faisceau de protons de 5x5  $m^2$ , une intensité de 0,5nA et 10 secondes d'intégration sur 100 plages différentes qu'avec un faisceau de 1x1mm<sup>2</sup>, une intensité de 10nA et un temps d'intégration de 1000s. Ces limites de détection (fig. 1) sont trop élevées par rapport aux teneurs à doser dans le blanc de plomb (tableau 1). Deux solutions sont envisageables afin de les abaisser : amincir la coupe, et/ou opérer avec un système de détection X en longueur d'onde, ce qui améliorera de un à deux ordres de grandeur les limites de détection en réduisant fortement la valeur du fond continu.



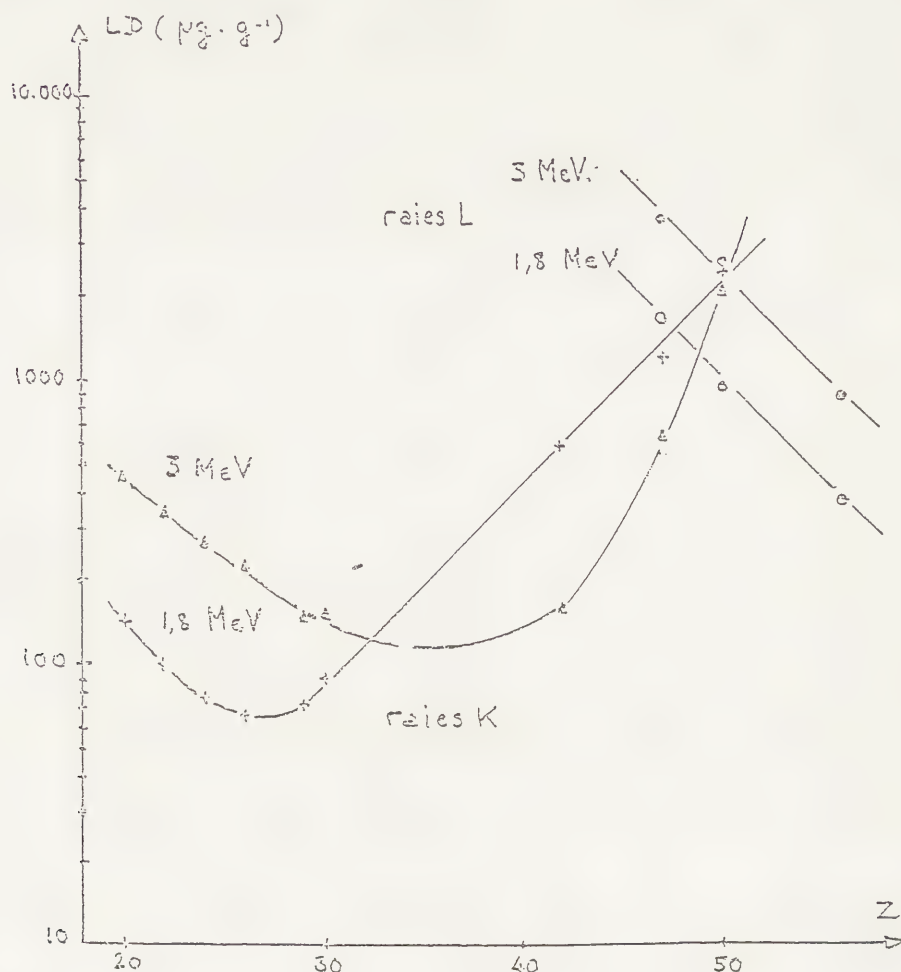


FIGURE 1

Limites de détection en fonction du numéro atomique de l'élément,  
dans le blanc de plomb.

$E_p = 1,8$  et  $3$  MeV  $C = 10 \mu C$   $I = 0,5$  nA

Faisceau de dimensions  $5 \times 5 \mu m^2$

TABLEAU 1

Teneurs en  $\mu g/g$ , pour quelques éléments,  
publiées par J.P.W. HOUTMAN et J. TURKSTRA /2/  
et limites de détection actuellement possibles avec la microsonde nucléaire  
utilisée, sur des microcouches de blanc de plomb.

Teneurs observées par activation neutronique					
Période	Ag	Cr	Cu	Mn	Zn
1500 - 1650	17 - 27	225 - 500	150 - 220	70 - 110	0 - 60
1650 - 1850		0 - 35			
1850 - 1940	0,5 - 20		0 - 60	0 - 12	0 - 60 sauf exceptions
1940 -	0,5 - 9				600 - 6000
Limites de détection autorisées avec la microsonde nucléaire	900	100	100	100	125

En dépit de ces limites de détection insuffisantes, et en cours d'amélioration, l'analyse ( $5 \times 5 \mu\text{m}^2$ ), protons de 3 MeV, 0,5 nA et 500s de neuf coupes de peinture du 15<sup>ème</sup> au 20<sup>ème</sup> siècle a permis de vérifier, par exemple, que les échantillons de le Nain et de David contiennent des teneurs en cuivre de l'ordre de  $200 \mu\text{g/g}$  valeurs qui correspondent à celles publiées par Houtman, alors que les échantillons prélevés sur des toiles de Delacroix, Courbet et Soutine en contiennent moins de  $100 \mu\text{g/g}$  (limite actuelle de détection). Ces mesures confirment bien la transition de 1820 (Alph., Giroux et Cie Paris)(3), et infirment l'observation des taux en argent et cuivre avancées par Kossolapov(5).

#### Mesure de la composition isotopique du Plomb par spectrométrie de masse

Le plomb naturel est composé de quatre isotopes de masse 204, 206, 207 et 208 dont les proportions à l'origine de la Terre sont mesurées actuellement dans certaines météorites. Cette composition a évolué avec le temps en raison de l'addition d'isotopes radiogéniques  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  et  $^{208}\text{Pb}$  issus respectivement de la désintégration radioactive de  $^{238}\text{U}$ ,  $^{235}\text{U}$  et  $^{232}\text{Th}$ .

Depuis une quinzaine d'années, la composition isotopique du plomb est déterminée par spectrométrie de masse avec une précision supérieure à  $10^{-3}$ . Ainsi d'après les données de BREVART (1985)(9) et de MARCOUX (1986)(10), le plomb des galènes d'Europe moyenne et méridionale présente des variations faibles du rapport  $^{206}\text{Pb}/^{204}\text{Pb}$  (fig.2) comprises entre 18.2 et 18.6 pour des rapports  $^{207}\text{Pb}/^{204}\text{Pb}$  quasiment constants ( $15.63 \pm 0.05$ ). Ces minéralisations sont issues d'une croûte continentale différenciée principalement il y a environ  $600.10^6$  ans. A l'inverse en Fenno-Scandinavie et en Ecosse, la différenciation de la croûte est beaucoup plus ancienne (de l'ordre de  $2000.10^6$  -  $2700.10^6$  ans) et les galènes y présentent d'importantes variations de composition isotopique (fig. 3) allant, par exemple, pour le rapport  $^{206}\text{Pb}/^{204}\text{Pb}$ , de 15.5 pour les minéralisations les plus anciennes à 37 pour les plus récentes (JOHANSSON et RICKARD, 1984(11) (12)).

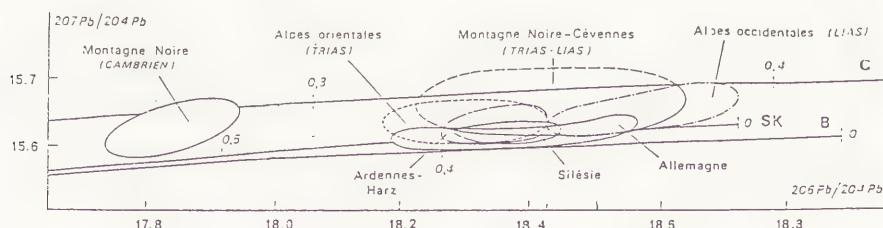


Fig. 2 Variations isotopiques du plomb des minéralisations de l'Europe moyenne et méridionale dont la croûte continentale s'est différenciée il y a environ  $600.10^6$  (d'après les données de BREVART (1985)(9) et MARCOUX (1986)(10). Trois courbes d'évolution isotopique théorique du plomb sont reportées comme références ; elles ont été calculées suivant les modèles de STACEY et KRAMERS (1975)(16) (courbe SK) et de ZARTMAN et DOE (1981)(17) (courbes B et C).

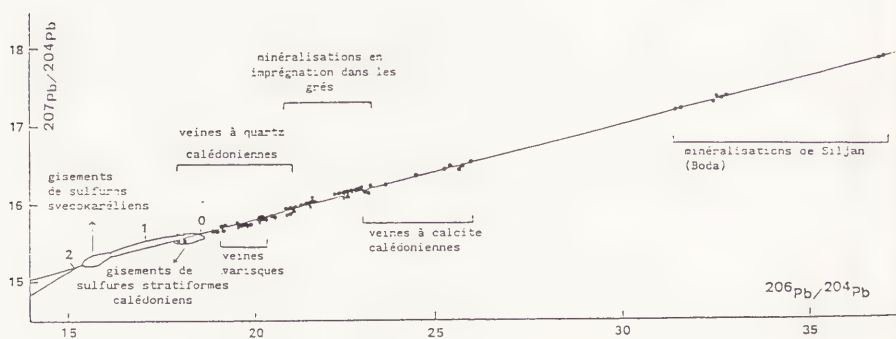


Fig. 3 Variations isotopiques en Plomb des minéralisations de Fenno-Scandinavie, dont la croûte continentale s'est différenciée au moins depuis 2000 Ma.



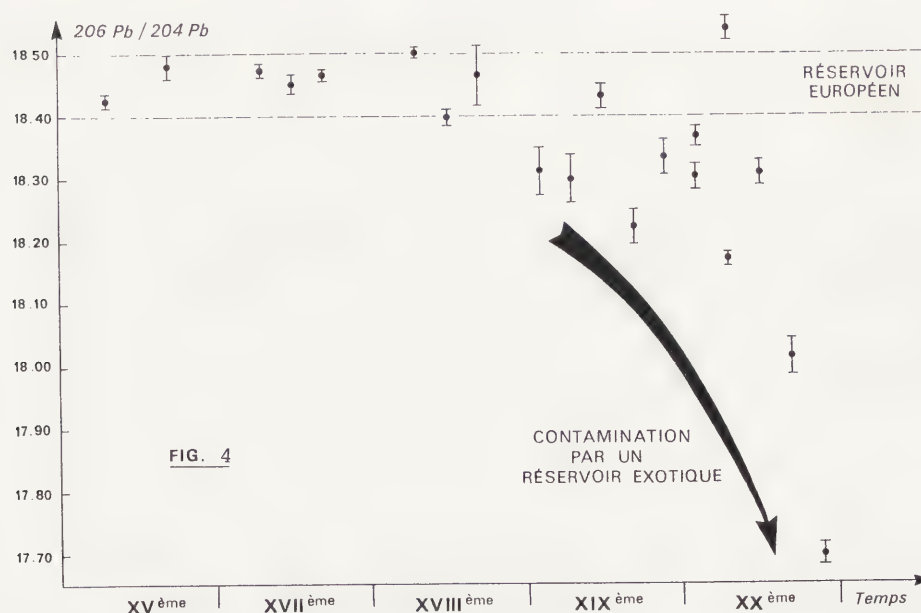
Epoque	Peintre	Ecole/Pays	$^{206}\text{Pb}/^{204}\text{Pb}$ corrigé de la d.M.
XVe	Neri di Bicci	Florence	$18.426 \pm 0.011$
XVe	Mateo di Giovanni	Sienna	$18.479 \pm 0.019$
XVIIe	Le Brun	France	$18.473 \pm 0.009$
XVIIe	Van Peolenburg	Pays Bas	$18.453 \pm 0.015$
XVIIe	Van Goyen	Pays Bas	$18.467 \pm 0.007$
XVIIIe	Watteau	France	$18.503 \pm 0.005$
XVIIIe	Ecole Française	France	$18.398 \pm 0.012$
XVIIIe	Mengs	Allemagne	$18.468 \pm 0.056$
XVIII-XIXe	David	France	$18.314 \pm 0.006$
XIXe (2e moitié)	Moreau	France	$18.301 \pm 0.042$
1855	Courbet	France	$18.434 \pm 0.017$
1863-1867	Collect. Pasteur	France	$18.223 \pm 0.036$
1879	Manet	France	$18.358 \pm 0.010$
1910-1912	R. Delaunay	France	$18.306 \pm 0.020$
1922	Soutine	France	$18.368 \pm 0.006$
1923-1934	Kupka	France	$18.172 \pm 0.009$
1937	Valmier	France	$18.542 \pm 0.017$
1946	de Chirico	France	$18.316 \pm 0.022$
1985	Ech. Ind. HB et B	Pays Bas	$18.010 \pm 0.013$
1985	Ech. Ind Heubach et Lindgens	R.F.A.	$17.692 \pm 0.016$

Tableau 2 Composition isotopique en plomb des blancs de plomb réalisés à Montpellier au Laboratoire de Géochimie Isotopique sur un spectromètre de masse à source thermoionique CAMECA TSN 206S. Les rapports  $^{206}\text{Pb}/^{204}\text{Pb}$  sont corrigés de la discrimination de masse.

KEISCH (1970)(13) et KEISCH et CALLAHAN (1976)(14) ont observé une variation des compositions isotopiques du plomb extrait du blanc de plomb à partir de 1820. Cette variation s'observe particulièrement dans les blancs de plomb utilisés par les peintres anglais au XIXe et au XXe siècle. Le Laboratoire de Géochimie Isotopique de l'Université de Montpellier II a mis au point un protocole expérimental permettant d'opérer en routine sur des prélèvements de blanc de plomb inférieurs à 0.1 mg ; l'analyse isotopique s'effectue sur un spectromètre de masse à source thermoionique CAMECA TSN 206S. Chaque analyse correspond à un dépôt de 0.2 µg de Pb sur un filament de Rhénium suprapur préalablement dégazé sous vide à 2000°C. La précision sur le rapport  $^{206}\text{Pb}/^{204}\text{Pb}$  est supérieur à  $10^{-3}$  après correction de la discrimination de masse.

Vingt échantillons de blanc de plomb, couvrant la période du XVe au XXe siècle, ont été analysés (tableau 2). Ces nouvelles données confirment et précisent les résultats antérieurs. Elles montrent en effet :

1°/ que du XVe au XVIIIe siècle inclus, les peintures européennes réalisées en France, aux Pays-Bas et en Italie présentent une composition isotopique en Pb très homogène (fig. 4) caractéristique d'un réservoir européen (REU) présentant un rapport  $^{206}\text{Pb}/^{204}\text{Pb}$  égal à  $18.45 \pm 0.05$ .



Cette source se trouve dans les minéralisations plombifères de la croûte continentale d'Europe moyenne et méridionale, exploitées à cette époque en Allemagne, en Autriche, en France, en Espagne, en Italie et dans le Sud de l'Angleterre.

2°/ qu'au XIXe et au XXe siècles, apparaît progressivement une anomalie isotopique se traduisant par l'apparition d'un plomb moins radiogénique, c'est-à-dire par des rapports  $^{206}\text{Pb}/^{204}\text{Pb}$  nettement inférieurs à ceux du réservoir européen (fig. 4). Cette anomalie est provoquée par le mélange du plomb du réservoir européen (REU) avec celui d'un réservoir exotique (REX).

Ce dernier correspond à un plomb de galène(s) ancienne(s) d'âge supérieur à 600.106 ans formée(s) au sein d'une croûte continentale différenciée précocement dans l'histoire de la Terre. On note l'addition croissante du plomb REX au plomb REU du XIXe au XXe siècle ; ainsi, parmi les échantillons analysés, les blancs de plomb fabriqués aux Pays-Bas et en R.F.A. en 1985, présentent les rapports  $^{206}\text{Pb}/^{204}\text{Pb}$ , les plus faibles compris entre 18.00 et 17.70. Ce mélange progressif, avec domination de plus en plus forte du plomb REX, correspond vraisemblablement à la fermeture de grandes mines européennes au XIX et surtout au XXe siècle et d'autre part à l'importation massive de minéral en provenance de terrains antécambriens d'Amérique du Nord et d'Australie via l'Angleterre.

3°/ suivant cette interprétation, les résultats obtenus sur 19 peintures norvégiennes du XIIIe au XVe siècles (PLAHER, (1976) (8) 18.38  $^{206}\text{Pb}/^{204}\text{Pb}$  18.50) ont très peu de chance de provenir de blancs de plomb formés à partir de galènes fennoscandinaves ; une origine européenne (plomb REU) est tout à fait vraisemblable.

La spectrométrie de masse et la microsonde nucléaire donnent des résultats complémentaires pour la datation et l'authentification des peintures. Le rapport isotopique du plomb,  $^{206}\text{Pb}/^{204}\text{Pb}$ , mesuré dans des microprélèvements de blanc de plomb pur ou en mélange par spectrométrie de masse, reste constant jusqu'au début du 19ème siècle puis diminue par apport du plomb "exotique". Un plus grand nombre d'analyses permettra de préciser l'évolution de la composition isotopique en relation avec la date et l'origine géographique des oeuvres. L'analyse des impuretés du blanc de plomb par microsonde nucléaire sur des coupes de peinture permettra d'affiner la datation à partir de séquences chronologiques de compositions distinctes.

#### BIBLIOGRAPHIE

1. Bego P. et Vercier P., Monographie de Muséologie, (4ème année de l'Ecole du Louvre), "Etude Scientifique d'une Ecole ou d'un peintre primitif, classique ou moderne. Préciser l'apport des méthodes optiques, physico-chimiques, informatiques de Laboratoire à la connaissance des oeuvres. Limites actuelles, possibilités de cette approche : blanc de plomb, blanc de titane." (1986).
2. Houtman et Turkstra, "Neutron activation analysis of trace elements in white lead and the possible application for age determination of paintings", International Atomic Energy Agency, Symposium on radiochemical methods of analysis, (Salzburg, Austria, 19/23 October, 1964).
3. Kuhn, "Trace elements in the white lead and their determination by emission spectrum and neutron activation analysis", Studies in Conservation, vol. II n°.4, novembre 1966.
4. Steinnes, "Trace elements in the white lead from medieval altar frontals determined by activation analysis", Universitetes olosaksamlings'arbok, 1972-1974, (Oslo 1976) pp 139-140.
5. Kossolapov et Sizov, "Impurities in white lead and the metallurgy of lead", ICOM Committee for Conservation Preprints, 7th Triennial Meeting, Copenhagen, 10-14 September 1984.
6. Nens, Trocellier, Engelmann, Lahanier, "Analyse de la composition élémentaire de coupes de peinture par microsonde électronique", ICOM Committee for Conservation Preprints, 7th Triennial Meeting, Copenhagen, 10-14 September 1984.



7. Nens, Trocellier, Engelmann, Lahanier, "Sample analysis of masterpieces and archeological materials by nuclear microprobe principle, possibilities, preliminary results", Nuclear Instruments and Methods in Physics Research, Amsterdam 1986.
8. Plaher, "Isotopes ratios of lead as source identification in pigments from Norwegian Medieval Art with some comments on trace elements composition of white lead", Universitetes oldsaksamling' arbok, 1972-74, Oslo, 1976, pp 136-138.
9. Brevart, O., "Les isotopes du plomb en métallogénie, Thèse Univ. Paris VII, 477 p. (1985).
10. Marcoux, "Isotopes du plomb et paragenèses métalliques traceurs de l'histoire des gîtes minéraux", Univ. Clermont-Ferrand, II, 300 p. (1986).
11. Johansson A., Rickard D., "Isotopic composition of Phanerozoic ore leads from the Swedish segments of the Fennoscandian shield, Mineral. Deposita 19, 1984, 249-255.
12. Parnell J. et Swainbank I., "Galena mineralisation in the orcadian basin, Scotland : Geological and isotopic evidence for sources of lead", Mineralium Deposita 20, pp 50-56. (1985).
13. Keisch B., "On the use of isotope mass spectrometry in the identification of artists' pigments, Studies in Conservation, 15, 1-II, 1970.
14. Keisch B., Callahan R.C., "Lead isotope ratios in artists' lead white : a progress report", Archaeometry 18, 2, 1976, pp. 181-193.
15. Brill R., Shields W., Wampler J., "New direction in lead isotope research, Application of Science in examination of works of art, W.J. Young ed., 1970, pp. 73-83.
16. Stacey J.S., Kramers J.D., "Approximation of terrestrial lead isotope evolution by a two stage model", Earth Planet. Sci. Lett. 26, 1975, pp. 207-221.
17. Zartman R.E., Doe B.R., "Plumbotectonics. The models." Tectonophysics 75, 135-162, 1981.





## SUMMARY

Ornamented columns of a temple hall were investigated by reflectography and emissiography. The temple is supposed to have been built in the twelfth century and contains three wall paintings and four ornamented columns. But the paintings and columns are entirely darkened now. Research revealed many figures which could not be found either with the naked eye or by an infrared film. While reflectograms showed skillful and powerful drawings, emissiograms indicated the painting technique and pigment used. The study still being continued will certainly produce an important result for Japanese art history.

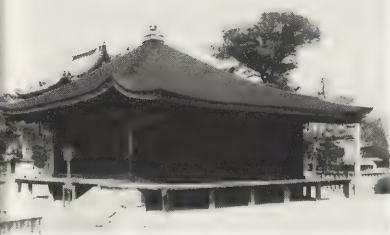


Photo 1 The exterior of Taishidō

## EMISSIOGRAPHY AND REFLECTOGRAPHY OF ORNAMENTED COLUMNS

Sadatoshi Miura  
Conservation Scientist  
Tokyo National Research Institute of Cultural Properties  
Conservation Science Department  
13-27 Ueno Park, Taito-ku, Tokyo, JAPAN 110

Introduction

Staff of the Tokyo National Research Institute of Cultural Properties carried out research on the paintings of a medieval temple in Japan by using an infrared television camera. The system used was explained at the last ICOM meeting in Copenhagen.<sup>(1)</sup> In this report, the study of column paintings by reflectography and emissiography will be mentioned with some illustrations. The investigation was made in March, 1986 at Kakurinji Temple at Kakogawa.

Kakurinji Temple is located at Kakogawa city, Hyōgo prefecture. According to a biography of the temple, it is said that the temple was founded in 583 by Prince Shōtoku as a temple dedicated to Buddha and the four heavenly kings. Most of the buildings still remaining now were constructed in later periods, from the twelfth to sixteenth centuries, the golden age of the temple.

Taishidō (a hall consecrated to Prince Shōtoku) is one of the most important national treasures at the temple. From an inscription discovered on a shingle during the restoration of the hall in 1918, Taishidō is supposed to have been constructed in 1112.

Taishidō is a single storey, 5.4m wide, 7.2m deep and 7.5m high building. It contains four ornamented columns at the corner of a platform and three wall paintings (Fig.1): Prince Shōtoku, 'Kubon Raigō' (representing nine figures of Amida Buddha coming down to welcome spirits of his believers) and 'Nehan' (Buddha at his death). Since the image of Prince Shōtoku painted on the south-east wall is stored in a small shrine, the painting is well conserved. However, two other paintings drawn on both sides of the rear wall of the platform have become dark. An infrared photography taken by a priest of the temple revealed the images in 1976. The discovery attracted public attention.

Infrared photography, however, found only some figures on the four ornamented columns. From 1985 to 1986, research was carried out by the author's group to study the iconography of the painting. Main investigation was conducted from March 24 to April 3, 1986.

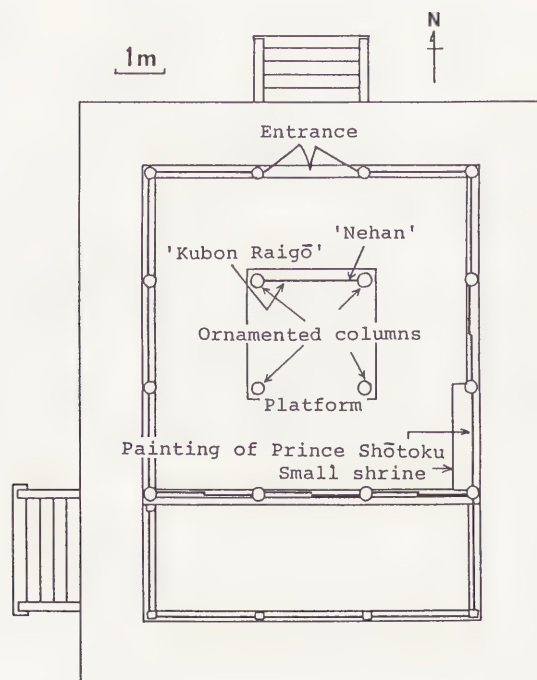


Fig.1 Plan of Taishidō

### Set-up

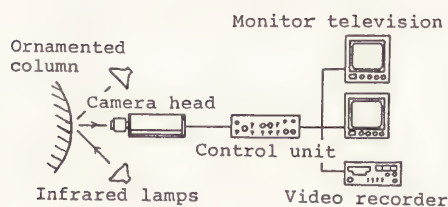


Fig.2 Diagram of the apparatus for the reflectography

#### 1. Reflectography

The system consisted of two infrared lamps, a camera head with an infrared vidicon tube (Hamamatsu, N214-06), a video recorder and a tripod for the lamps and the camera head.

The ornamented columns are poles of 1.7m height from the platform with a radius of about 13cm. To minimize deformation, the area of the camera was limited to quite a small area (13 X 18cm) and reflectograms were taken overlapping each other. As a result, the number of reflectograms of one column painting reached more than a hundred.

#### 2. Emissiography

The condition of emissiography was as follows: <sup>(2)(3)(4)(5)</sup>

Voltage: 200kV

Ampere: 5mA

Distance: 0.4m

Time: 15minutes

Filter: tin plate (3mm thick)

Apparatus: Philips G301

Film: Fuji FG (an emulsion on a single surface)

The film was fixed to a surface of the column by a transparent plastic cover. All work was carried out in the night, because a bare film is used for emissiography.

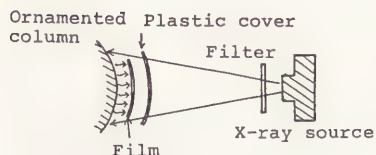


Fig.3 Diagram of the apparatus for the emissiography



Fig.4 Presumed original figure of Acala (by Hayashi)



Photo 2 Reflectogram of Kimkara

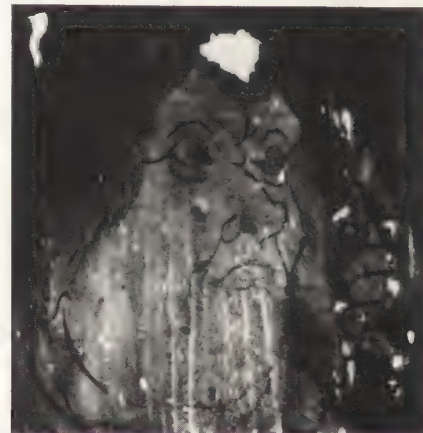


Photo 3 Reflectogram of Cetaka



Photo 4 Emissiogram of Kimkara and Cetaka



### Result

The results of the investigation are now being examined thoroughly by Miss Yanagisawa, chief of the research group and former director of the Department of Art History of the Institute. In this chapter, one of the evident results will be mentioned.

While a figure of Acala was found on the north-east column (Fig.4), a sword around which a dragon is winding, symbol of Acala, was revealed on the north-west column. In addition, two attendants of Acala, Kimkara and Cetaka, were discovered on the north-west column (Photo 2 and 3). Although both columns are entirely darkened, the reflectograms show skillful and powerful drawings unable to be seen either with the naked eye or by an infrared film.

A sutra iconographically prescribes white flesh for Kimkara and red flesh for Cetaka. The shading noticed on the emissiogram of Kimkara (Photo 4) may be due to a brushing technique of a pigment which consists of a heavy element, red lead or vermillion, on a white pigment, probably oyster shell white. The flesh of Cetaka, however, is transparent on the emissiogram. If the two attendants were colored according to the sutra, Cetaka should have been painted with a red pigment of a light element, red ochre for example. But the pigments have not yet been identified.

It is supposed that these figures were drawn to protect the sacred hall from invaders. Especially, the figure of Acala, guardian of ascetic devotees, watches the direction of the entrance of Taishidō. But compared with other paintings of Acala, an Acala image looking to his left is unusual. This is one of the iconographical subjects that our research has brought up for study by Japanese art historians.

### Acknowledgement

The author would like to express his thanks to Mr.Yoshida, the chief priest of Kakurinji Temple, and his colleagues, Prof.Akiyama, Gakushūin University, Miss Yanagisawa and Mr.Nokubo, Tokyo National Research Institute of Cultural Properties, Prof.Donohashi, Kōbe University and Mr.Hayashi, Keiō University. He is also grateful to Mrs.Matsubara for her kind help in accomplishing this paper.

### NOTES

1. S.Miura, "Design of the Portable Apparatus of an Infrared Television Camera" (Paper delivered at the Seventh Triennial Meeting of ICOM Committee for Conservation, Copenhagen, September, 1984), pp.75-76
2. S.Miura, "Emissiography of the Painting by Kuroda", Kobunkazai no Kagaku (Scientific Papers on the Japanese Antiques and Art Crafts) 30(1985), pp.21-27 (in Japanese)
3. C.F.Bridgeman, S.Keck, H.F.Sherwood, "The Radiography of Panel Paintings by Electron Emission", Studies in Conservation 3(1958) pp.175-182
4. S.R.Delbourgo, "Two Far Eastern Artefacts Examined by Scientific Methods", Conservation of Far Eastern Art Objects, (Tokyo: Tokyo National Research Institute of Cultural Properties, 1980), pp.163-179
5. F.Drilhon, "L'apport de l'emissigraphie dans l'etude des peinture et des émaux" (Paper delivered at the Seventh Triennial Meeting of ICOM Committee for Conservation, Copenhagen, September, 1984), pp.54-57





## RESUME

## REALISATION ET ETUDE PAR MICROSCOPIE ELECTRONIQUE ANALYTIQUE EN TRANSMISSION DE COUPES ULTRA-FINES D'ECHANTILLONS DE PEINTURES

La technique d'impregnation-inclusion dans une résine epoxy, suivie d'une ultra-microtome, permet d'obtenir des coupes stratigraphiques et des prélèvements de peinture d'une épaisseur inférieure à 100nm. L'étude morphologique des pigments par microscopie Electronique en transmission est suivie de leur reconnaissance chimique par Spectrométrie des Rayons X complétée de leur identification structurale par microdiffraction des Electrons. Une première application réalisée sur "La Serpente de bois" d'E. Manet a aussi permis de caractériser sans ambiguïté le bleu de cobalt, l'outremer et le blanc de plomb (hydrocéruse). Par contre, le caractère non stoechiométrique du jaune de Naples n'a pas permis de mettre en relation directe ses paramètres cristallins mesurés avec ceux des standards décrits dans les fichiers classiques.

M.C. PAPILLON(1), R. LEFEVRE(1)  
Ch. LAHANIER(2), A. DUVAL(2), J.P. RIOUX(2)

- (1) Laboratoire de Microscopie Analytique Appliquée aux Sciences de la Terre, Université Paris XII. F-94010 CRETEIL.
- (2) Laboratoire de Recherche des Musées de France, Palais du Louvre. F-75041 PARIS Cédex 01.

## 1 - INTRODUCTION

Les prélèvements effectués sur les oeuvres d'art, en particulier les peintures, en vue d'étudier leur composition chimico-minéralogique, sont nécessairement limités en poids et en volume, sinon ils dégraderaient irrémédiablement l'oeuvre.

L'étude de la composition de ces petits prélèvements doit donc mettre en oeuvre des techniques de microcaractérisation, parmi lesquelles la microscopie analytique joue un rôle primordial. Elle allie en effet plusieurs types de performances tout à fait adaptées à ce genre d'objets : un procédé analytique peu ou pas destructif, une sensibilité à de très faibles teneurs en éléments chimiques présents dans de très petits volumes (analyse de traces), enfin, une localisation précise (dans la gamme des micromètres, voire des nanomètres) de la couche analysée ou d'une zone d'intérêt au sein d'une couche déterminée.

L'application de ces méthodes de microscopie analytique nécessite une préparation préalable des microprélèvements car ils devront généralement être soumis à des vides ou à des potentiels électriques importants. Or, ils peuvent contenir des matières volatiles (par exemple de l'eau) et sont le plus souvent isolants (sauf les métaux). De plus, certaines techniques de microanalyse chimique (sonde électronique, analyseur ionique) exigent un excellent état de surface obtenu par polissage soigné de l'échantillon. Du fait, d'une part, de la dureté généralement assez grande des grains minéraux pigmentaires et, d'autre part, du durcissement avec le temps des différents liants (huiles, siccatifs, vernis) qui unissent ces grains, un prélèvement effectué sur un tableau ou une fresque est généralement préparé par polissage, comme s'il s'agissait d'un échantillon minéralogique ou pétrographique. Cependant, cette dureté minérale globale n'exclut pas une grande hétérogénéité d'une couche à l'autre (ou au sein d'une même couche) et une grande friabilité du fait du caractère plus ou moins lâche des liaisons existant entre les grains minéraux.

Dureté hétérogène et friabilité expliquent ainsi l'échec d'un grand nombre de tentatives de polissage d'échantillons picturaux. On peut, cependant, améliorer sensiblement les résultats de ces essais, en procédant à l'inclusion-enrobage préalable du microprélèvement dans une résine. En fait, même après une telle opération, il est rare qu'il ne subsiste pas des dépressions ou des reliefs à la surface de l'échantillon ou que certaines couches (le gesso par exemple) ne disparaissent pas par dissolution ou effritement dans les liquides utilisés lors du polissage.

C'est pour tenter de pallier ces différents inconvénients que nous avons décidé de préparer un prélèvement de peinture comme un échantillon biologique, c'est-à-dire, non pas simplement en l'incluant (ou en l'enrobant) mais en l'imprégnant intimement de résine et non pas en le polissant mais en le sectionnant finement. Ce faisant, non seulement sa cohésion, et donc son intégrité tout au long de l'analyse, sont renforcées, mais encore, toutes les possibilités de la Microscopie Electronique en Transmission Analytique (META) deviennent accessibles, alors que seules celles de la Microscopie Electronique en Balayage Analytique (MEBA) le sont aux échantillons massifs qu'ils soient polis ou non.

Nous nous proposons donc d'exposer dans les lignes qui suivent les méthodes d'imprégnation des échantillons et de confection de coupes ultra-fines, ainsi que quelques exemples des premières applications que nous avons réalisées.

## 2 - IMPREGNATION, INCLUSION-ENROBAGE ET ULTRAMICROTOMIE DES ECHANTILLONS DE PEINTURES.

Afin d'augmenter la résistance des échantillons de peintures aux contraintes engendrées par la microtomie, il est nécessaire non seulement de les inclure (ou enrober) dans une résine, mais surtout de faire pénétrer celle-ci intimement, à coeur. La résine doit donc être extrêmement fluide lors de l'imprégnation et présenter, après polymérisation, une dureté proche de celle du fragment à couper. De plus, sa composition chimique ne doit pas interférer avec celle du fragment à microanalyser.

Divers essais ont montré qu'un mélange de SPURR (1) de dureté moyenne satisfaisait à ces diverses exigences (fluidité, dureté appropriée, neutralité chimique). Il s'agit d'une résine Epoxy qui polymérise de façon uniforme (sans rétraction), qui est stable sous le faisceau électronique et qui ne contient que des éléments organiques (C, N, O...), à l'exclusion de tout élément minéral. Nous l'avons préparée selon les proportions suivantes : Résine (ERL 4206 ou VCD) : 10 ml; Plastifiant (DER 736) : 6 ml; Durcisseur (NSA) : 26 ml; Accélérateur (DMAE) : 0,4 ml.

Cette résine n'est pas hydrosoluble, ce qui rend indispensable la déshydratation préalable des échantillons. Cependant, la teneur en eau libre des prélèvements picturaux étant pratiquement nulle, on se borne à placer ceux-ci 24h dans une étuve à 40°C. L'imprégnation des fragments se fait à température ambiante (20°C), pendant au moins 12 h, par une résine fraîchement préparée. Les échantillons imprégnés sont ensuite transférés pour inclusion dans des capsules de polyéthylène et noyés dans la même résine. On les maintient dans une position telle qu'ils se présenteront ensuite transversalement au couteau de l'ultramicrotome. Les capsules, fermées, sont placées à l'étuve à 40°C pendant 4 à 5 jours, pour polymérisation.

L'ultramicrotomie débute par la mise à l'affleurement du fragment par taille au rasoir de la résine environnante en pyramide tronquée. A l'aide d'un ultramicrotome à avance mécanique muni d'un couteau de verre, on débite l'échantillon en coupes semi-fines (5 à 10 µm) ou fines (1 à 2 µm) que l'on peut observer au Microscope Photonique, au Microscope Electronique à Balayage (MEB), éventuellement équipé d'une Sonde Electronique, ou encore analyser par Emission Ionique Secondaire. Il est possible d'obtenir soit par avance mécanique, soit par avance thermique du microtome, des coupes beaucoup plus minces dites ultrafines (couramment de 100 à 150 nm, voire de quelques dizaines de nanomètres dans les cas favorables). Ces coupes ultra-fines, perméables aux électrons, sont étudiées par Microscopie Electronique en Transmission Analytique (META). Selon la nature de l'échantillon de peinture, en particulier s'il renferme des grains minéraux très durs, il peut être nécessaire de remplacer le couteau de verre par un couteau de diamant.

Les coupes ultra-fines destinées à l'étude par META sont recueillies sur un bain d'eau et placées sur une grille métallique spéciale (en Cu, Al ou Au) dont on choisit judicieusement la dimension des mailles, lesquelles peuvent être marquées afin de faciliter le repérage de zones déterminées. Enfin, la coupe est rendue conductrice par évaporation sous vide d'un mince film de carbone.

## 3 - LA MICROSCOPIE ELECTRONIQUE EN TRANSMISSION ANALYTIQUE (META) (fig. 1)

Comme il a été dit plus haut, tout l'intérêt d'obtenir des coupes ultra-fines de fragments de peintures, tient dans le fait qu'étant suffisamment minces pour être perméables aux électrons, on peut les étudier par Microscopie Electronique en Transmission (morphologie des grains à très fort grossissement, granulométrie, relations entre les grains, comptage, traitement automatique des images ...). De plus, un Microscope Electronique à Transmission peut être équipé de moyens analytiques par Spectrométrie des Rayons X émis sous le faisceau d'électrons (Microsonde Electronique de Castaing) : les coupes ultra-fines se prêtent particulièrement bien à ce type d'analyse car les calculs de correction sont alors très réduits. Enfin, des données structurales essentielles à la caractérisation minéralogique des grains de pigments sont facilement obtenues par l'interprétation des diagrammes de Microdiffraction Electronique. On obtient ceux-ci par l'interposition d'un diaphragme sur le trajet des mêmes électrons qui servent à la Microscopie et à la Microanalyse.

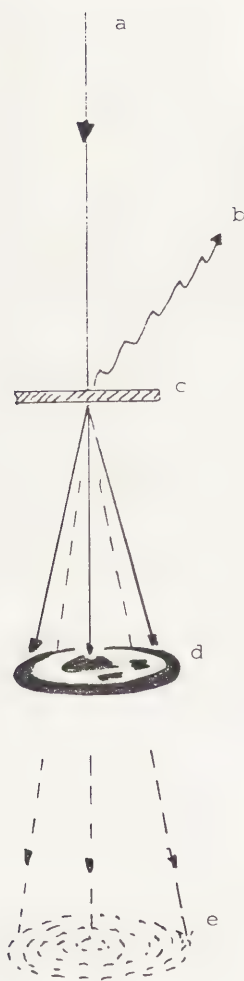


Fig. 1 - Schéma de principe de la Microscopie électronique en Transmission Analytique (META)

- a - Electrons incidents
- b - Rayons X émis : micro-analyse chimique par
  - Sélection des Energies (diode Si - Li)
  - Spectrométrie de longueur d'onde (cristaux)
- c - Coupe ultrafine (100 150 nm)
- d - Electrons transmis : image. (morphologie, granulométrie, comptage, localisation).
- e Electrons microdiffractés : diagramme. (structure cristallographique)



Nous avons utilisé un Microscope Electronique à Transmission JEOL 100 C équipé d'un microanalyseur par Sélection des Energies des Rayons X EDAX 711 (a). Celui-ci fournit une analyse chimique quantitative des silicates exprimée en poids d'oxydes comme cela est classique dans la littérature minéralogique. Pour les minéraux non silicatés, une analyse qualitative est seule fournie. La microdiffraction électronique a permis de faire d'emblée la distinction entre les minéraux amorphes (verres) et les minéraux cristallisés. Les diagrammes obtenus sur les seconds permettent généralement de les placer dans les grands systèmes cristallins et ainsi de conforter le diagnostic fondé sur la seule analyse chimique obtenue précédemment.

Pour la détection d'éléments chimiques en faibles teneurs, la Sélection des Energies des Rayons X, méthode qui a l'avantage de la rapidité, doit être relayée par la Dispersion des longueurs d'onde de ces mêmes Rayons X au moyen de Spectromètres à cristaux, méthode plus lente mais plus sensible. C'est donc à elle que nous avons eu recours pour tenter de détecter les éléments chimiques présents dans la pellicule superficielle de grains de Rutile traité (Microsonde Electronique CAMEBAX, CAMECA)(b)(2).

Enfin, pour distinguer de façon précise les formes cristallisées des différents pigments, nous avons eu recours à un autre Microscope Electronique à Transmission JEOL 100C(c) muni d'une platine goniométrique eucentrique permettant le déplacement et la rotation du grain étudié dans les trois directions de l'espace.

#### 4 - PREMIERES APPLICATIONS.

La méthode décrite ci-dessus a été appliquée à deux types d'échantillons picturaux :

- des prélèvements effectués sur une toile d'Edouard Manet : "La Serveuse de Bocks" (Musée d'Orsay, Paris)
- des poudres de Rutile et Anatase (Blancs de Titane) purs ou traités, fournis par Lefranc-Bourgeois (Le Mans, France).

Les résultats de cette deuxième étude sont présentés par ailleurs dans ce même volume (2).

Le petit échantillon prélevé dans la chemise bleu-verdâtre du fumeur situé au premier plan (fig.2) a été imprégné, coupé et analysé. Ce micro-prélèvement a été étudié dans le cadre d'une série d'analyses destinées à identifier les pigments utilisés et à comparer ces résultats avec ceux obtenus sur d'autres tableaux de Manet peints à la même époque et sur le même thème. Les personnages et détails représentés dans la "Serveuse de Bocks" présentent de grandes similitudes avec ceux de "Coin de Café-concert" (Londres, National Gallery) et "Café-concert" (Baltimore, The Walters Art Gallery) qui ont séparément fait l'objet d'études détaillées (3, 4, 5). Ces rapprochements soulèvent la question du lien exact entre ces oeuvres. Dans cette perspective les analyses en cours sur la "Serveuse de Bocks" paraissent particulièrement intéressantes.

Fig. 2 - Manet, "La Serveuse de Bocks", Musée d'Orsay, Paris. Emplacement du prélèvement étudié.



(a) Les manipulations ont été effectuées au Laboratoire d'Etude des Particules Inhalées du Département de Paris. Nous remercions A. GAUDICHET et M.A. BILLON-GALLAND pour leur collaboration expérimentée.

(b) Dans le Service Commun de Microanalyse Electronique de l'Université Paris XII, à la Faculté de Médecine de Créteil. Les manipulations ont été effectuées par P. BOUMATI que nous remercions vivement.

(c) Au Laboratoire de Minéralogie-Cristallographie de l'Université Paris VI. Les diagrammes de diffraction ont été réalisés par M. GANDAIS qui nous a fait profiter de sa très grande expérience de la Microdiffraction Electronique.



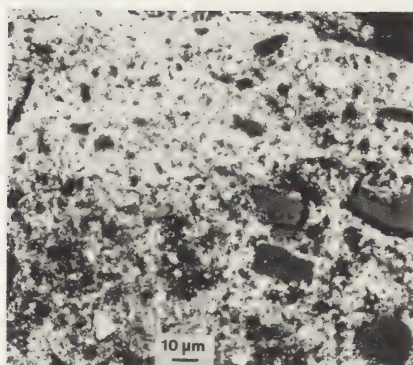


Fig. 3 - Image d'une coupe épaisse de l'échantillon au MEB (électrons rétrodiffusés).

Couleurs	Éléments décelés
<u>Majeures</u>	
Blanc	Pb
Bleu 1	Co et Al
Bleu 2	Na et Si
<u>Mineures</u>	
Jaune clair	Pb et Sb
Noir	Ca et P
Ocre jaune	Fe, Si, Al
Jaune orangé	Cd et S
Rouge carmin	Al, P, Pb
Vert vif	Cu et As
Vert sombre	Cr

Tableau 1 - Microanalyse électronique ponctuelle de grains de pigments sur coupe épaisse.

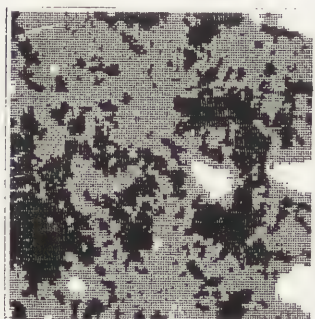


Fig. 4 - Image de répartition de Al (x360).

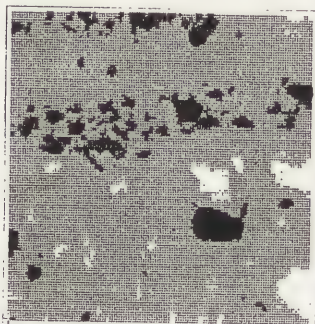


Fig. 5 - Image de répartition de Co (x360).

#### A Etude préliminaire : examen et analyse au MEB sur coupes épaisses

Sous l'objectif du microscope photonique, l'échantillon apparaît constitué d'une préparation blanche et d'une couche épaisse et hétérogène de matière picturale bleue. Dans cette dernière, les grains de pigments sont en grande majorité blancs et bleus. D'autres grains de couleurs vives et variées sont disséminés en faible quantité : jaune clair, jaune d'or, brun jaune, rouge, vert, noir.

Au moyen d'un MEB JEOL JSM 840 équipé d'un sélecteur des énergies des Rayons X ORTEC Système 5000, nous avons repéré sur des coupes épaisses (quelques centaines de µm) certains grains de pigments grâce à des images réalisées au moyen des électrons rétrodiffusés (fig.3). La détection ponctuelle, au sein de chacun des grains, des éléments chimiques associés permet, après interprétation, de caractériser la nature chimique des pigments. Le tableau 1 présente les résultats obtenus sur le même prélèvement.

Des cartes de répartition des éléments chimiques ont été réalisées par balayage de l'échantillon. Les fig. 4 et 5 présentent ainsi les localisations de Al et Co. Ces deux éléments, lorsqu'ils sont associés, indiquent la présence probable de bleu de cobalt.

#### B Apports de la Microscopie Electronique à Transmission Analytique (META) sur coupes ultra-fines

Deux coupes, d'une épaisseur estimée inférieure à 100 nm, déposées sur grille de cuivre ou d'or ont été analysées au MET. On constate dans ces coupes ultra-fines, des grains ou amas de grains dispersés et certains artefacts: déchirures de la résine, fracturation de certains grains, ainsi que des striations provoquées par les vibrations du couteau du microtome.

L'analyse des coupes ultra-fines a permis de discerner les pigments à partir de leur morphologie puis d'identifier un ou quelques grains par analyse élémentaire et diffraction d'électrons. L'analyse élémentaire permet de localiser des grains dont l'existence avait été préalablement mise en évidence au MEB. La diffraction d'électrons va permettre de les identifier très précisément à partir de leur structure cristalline.

##### a) Identification du bleu de cobalt

L'image révèle des amas de microcristaux allongés dont la taille est de l'ordre de 100 nm (fig 6). Ce matériau est relativement peu dense aux électrons. Le spectre d'émission X (fig 7) met en évidence les éléments du bleu de cobalt (Al, Co) ainsi que du plomb et du phosphore en faibles teneurs provenant probablement de l'excitation de la matière environnante. L'analyse par

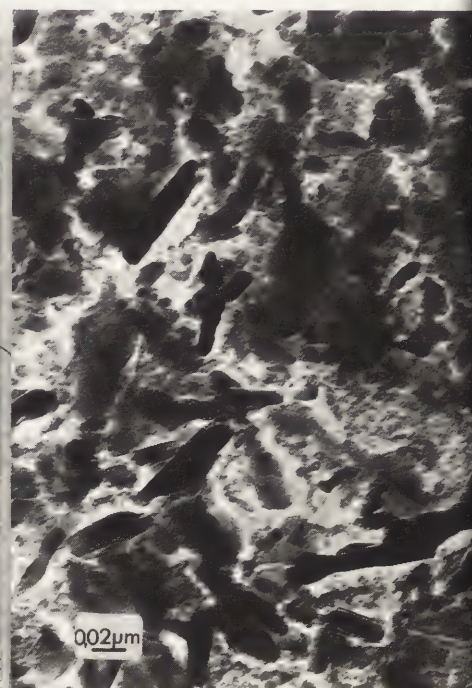


Fig. 6 - Image en MET d'un amas de microcristaux de bleu de cobalt.



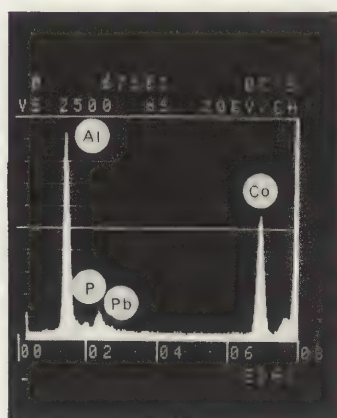


Fig. 7 - Microanalyse électronique des microcristaux de bleu de cobalt.



Fig. 8 - Diagramme de microdiffraction des électrons par les microcristaux de bleu de cobalt.

diffraction d'électrons sur des grains submicroniques (fig. 8) donne un diagramme de type Debye-Scherrer à raies continues qui correspondent effectivement à la structure atomique du bleu de cobalt de formule  $\text{Co Al}_2\text{O}_4$ . (ASTM 10-458).

b) Identification de l'outremer

L'image obtenue par transmission d'électrons (fig. 9) montre des grains de formes diverses, résultantes de l'orientation aléatoire des cristaux par rapport au plan de coupe. Cet aspect n'est pas observable sur coupe épaisse. La plupart des grains ont été fracturés par le couteau tout en conservant leur morphologie d'ensemble. Leur taille est ici de l'ordre du micron. Leur opacité est supérieure à celle du bleu de cobalt.

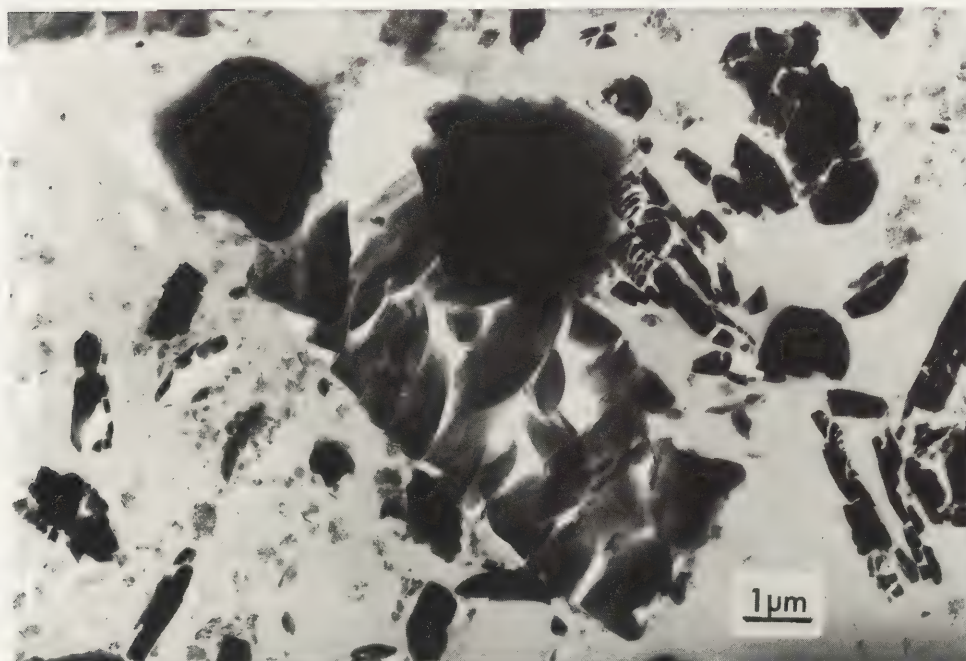


Fig. 9 - Image en MET d'un cristal fragmenté de bleu outremer.

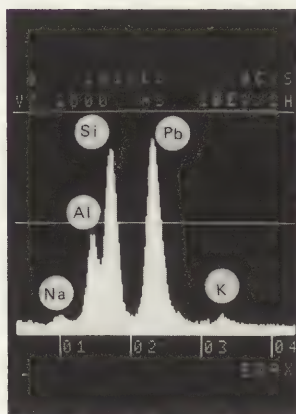


Fig.10 - Microanalyse électronique du cristal de bleu outremer de la Fig. 9.



Fig.11 - Diagramme de microdiffraction des électrons par le bleu outremer de la Fig. 9.

Le spectre d'émission X (fig. 10) comporte les raies K des éléments suivants : Na, Al, Si et K. Notons également la raie M du plomb dont la présence peut être expliquée par celle du blanc de plomb, présent également dans le matériau analysé. Le diagramme de diffraction d'électrons (fig.11) correspond aux fragments légèrement dissociés du mono-cristal de la fig. 9. Sa structure est celle de l'outremer de formule  $\text{Na}_{8,5}\text{Al}_6\text{Si}_8\text{O}_{28}\text{S}_4,3$  (ASTM 2-325). L'absence de soufre dans le spectre d'émission X est due à la superposition des raies K du soufre et M du plomb.

#### c) Identification du blanc de plomb

Les grains allongés de la partie supérieure du cliché de la fig. 12 sont très absorbants. De taille voisine du micron, ils se présentent sous forme de baguettes ou de sections carrées. Ce sont les grains les plus fréquemment observés, parfois regroupés. Le spectre d'émission X ne comporte que la raie M du plomb (fig. 13).

Le diagramme de diffraction d'électrons (fig. 14) effectué sur quelques grains voisins permet d'identifier l'hydrocérusite et non la cérusite. Les paramètres mesurés sur le diagramme de microdiffraction sont voisins de ceux rapportés sur la fiche ASTM 13-131 ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ).

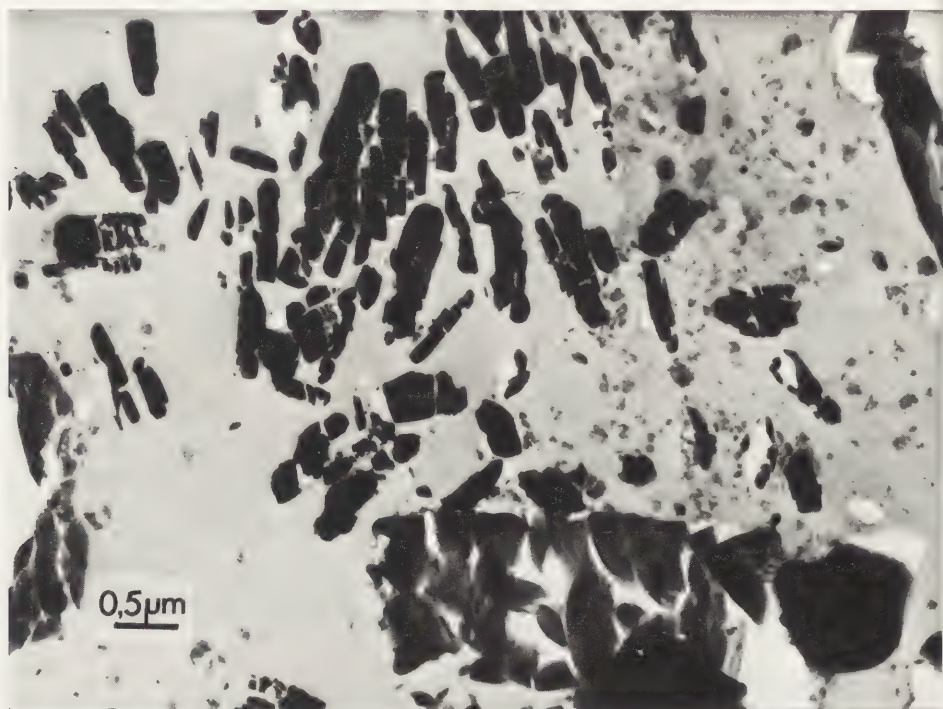


Fig. 12 - Image en MET de cristaux de blanc de plomb.



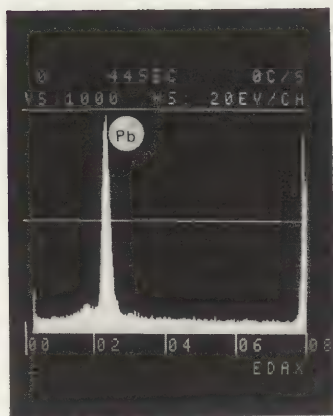


Fig. 13 - Microanalyse électronique des cristaux de blanc de plomb



Fig. 14 - Diagramme de microdiffraction des électrons par des cristaux de blanc de plomb.

d) Identification du jaune de Naples

Ces grains de dimension de l'ordre du micron et en faible concentration dans la couche picturale sont également très absorbants (fig.15). Le spectre d'émission X (fig. 16) met en évidence les raies M du plomb et L de l'antimoine. Le diagramme de

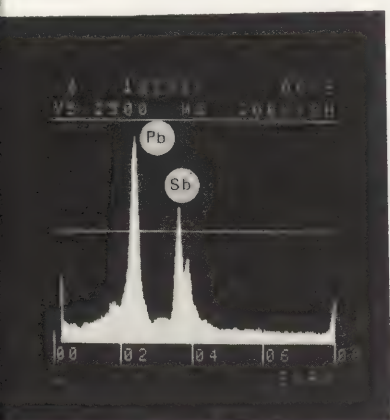


Fig. 16 - Microanalyse électronique des cristaux de jaune de Naples.

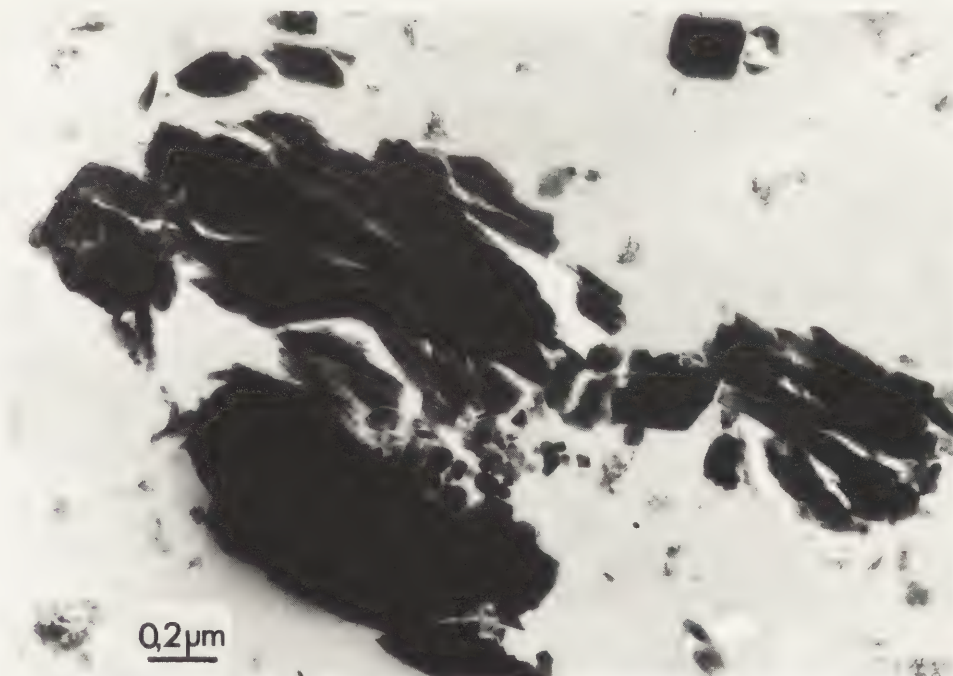


Fig. 15 - Image en MET de cristaux de jaune de Naples.



Fig. 17 - Diagramme de microdiffraction des électrons par des cristaux de jaune de Naples.

diffraction (fig. 17) ne correspond pas aux fiches ASTM 2-1375 et 18-687 de l'antimoniate de plomb. Ce composé non stoechiométrique a été utilisé dès l'Antiquité comme colorant des verres et glaçures puis en peinture sous l'appellation "jaune de Naples". Une analyse sur monocristal permettra ultérieurement de caractériser les paramètres cristallins de ce minéral synthétique.

L'identification partielle des constituants minéraux de cet échantillon de matière picturale de la "Serveuse de bocks" permet une première comparaison avec les résultats d'analyses effectuées sur les couleurs bleues des tableaux de scènes de Café-Concert conservés à Londres et à Baltimore.

Comme dans ces deux cas, plusieurs pigments bleus concourent à la réalisation de la couleur. Le bleu de cobalt et le bleu outremer ont effectivement été utilisés dans les trois oeuvres où ils sont mélangés à du blanc de plomb.

Deux différences se manifestent cependant dans "La serveuse de bocks" : le bleu céruléum décelé dans les deux autres tableaux n'y a pas été détecté (absence d'étain dans l'échantillon). Quant au jaune de Naples, il est absent des bleus de ces deux autres tableaux.

Bien que l'analyse ne soit pas encore exhaustive, il apparaît déjà que les principaux pigments sont identiques à ceux des bleus des deux autres tableaux. Cependant, des différences mineures mais significatives distinguent la couleur issue du tableau du Musée d'Orsay de celle des deux autres tableaux.

#### Conclusion

Cette étude ponctuelle montre quelques applications de cette technique à l'identification cristalline des pigments directement sur coupe. Il ne s'agissait pas ici d'effectuer l'analyse exhaustive de tous les pigments de la couche picturale mais d'illustrer l'intérêt d'appliquer cette méthode à la suite de l'analyse élémentaire en vue d'une identification structurale fine de certains pigments rendue difficile dans le cas de mélanges complexes. La microscopie électronique en transmission donne la taille et les caractéristiques morphologiques des pigments contrairement à l'image obtenue au MEB sur coupe épaisse par électrons rétrodiffusés ou secondaires.

Cette technique de préparation de coupes ultra-fines largement utilisée pour l'analyse des échantillons biologiques, nouvellement appliquée à l'analyse des peintures, requiert un savoir faire spécifique à la nature des échantillons de dureté hétérogène.

#### Références

1. A.R. Spurr, "A low-viscosity Epoxy Resin Embedding Medium for Electron Microscopy", *Journal Ultrastructure Research* 26, 3143 (1969)
2. C. Coupry, J. Le Marec, J. Corset, M.C. Papillon, R. Lefèvre, J. Riccarand, A. Duval, Ch. Lahanier, J.P. Rioux, "Analyse du blanc de titane appliquée à l'étude chronologique des peintures de chevalet", *Actes de la 8ème Réunion Triennale de l'ICOM CC*, (Sydney 1987)
3. Juliet Wilson Bareau, *The hidden face of Manet*, The Burlington Magazine (1986).
4. David Bomford et Ashok Roy, *Manet "The Waitress" - An investigation into its origin and development*, *National Gallery Technical Bulletin*, vol 7 (1983) pp 3-19
5. E. Melanie Gifford, *Manet's "At the Café" : Development and structure*, *The Journal of the Walters Art Gallery* (Baltimore, 1984)



## SUMMARY

A group of Royal and Great seals were examined with C-13 Fourier Transform Nuclear Magnetic Resonance (C-13 FTNMR) spectroscopy to determine the nature of their organic components by comparison with a series of control waxes and resins. Whilst the mediaeval examples contained only beeswax, the post mediaeval samples examined contained both wax and the resin colophony. This study showed that until the reign of George III beeswax was used, but then this alternated with other types of wax which may reflect availability of different sources of supply. Whilst colophony is present in all the early modern seals examined, it was noted that differences in colophony spectra between seals may be attributed to variations in source rather than deterioration or oxidation, allowing provenancing of such materials to be developed from this study.

## THE EXAMINATION OF ORGANIC COMPONENTS IN HISTORICAL NON-METALLIC SEALS WITH C-13 FOURIER TRANSFORM NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Don Robins, Analytical Consultant, 18, Chequers Square, Uxbridge Middx UB8 1NE England  
Alan Alstin, Conservation Department, Public Records Office, Portugal Street, London WC2A 3PH, England  
Dick Fletton, Glaxo Group Research, Greenford Road, Greenford, Middx UB6 0HE, England

Introduction

Seals attached to documents are valuable historical artefacts in their own right and whilst metallic seals have been studied extensively non-metallic seals have been comparatively neglected. Deterioration of many non-metallic seals in storage has prompted an interest in their conservation and repair which has concentrated upon the effects of deterioration rather than its causes (1), but the archival philosophy of sympathetic repair with modern materials matching historical counterparts has engendered a requirement for a detailed body of modern analytical data on these artefacts.

Our earlier report on the analysis of the organic components of a small group of mediaeval and early modern non-metallic seals with C-13 Fourier Transform Nuclear Magnetic Resonance (C-13 FTNMR) spectroscopy (2) was the first modern analytical approach after the pioneering work of Dobbie and Fox in 1914 (3). In this they found that a small number of varied seals (mainly personal and ecclesiastical) contained a mixture of beeswax and colophony (pine resin). Our study which concentrated upon Royal Seals showed that these early seals contained only beeswax and we detected resins only in the post-mediaeval seals. In the previous report we described the utility of C-13 FTNMR for such simultaneous analyses of unseparated organic mixtures and in this paper we discuss a more comprehensive analysis of a wider range of historical non-metallic seals which also serves to further develop the application of C-13 FTNMR to conservation science.

Analysis of Organic Components with C-13 FTNMR

Preliminary analyses of the organic components with infrared spectroscopy (5) demonstrated that discrimination between resins and waxes in mixtures with this technique was problematic. The reasons for employing C-13 FTNMR were outlined in our previous reports (2,5) but since this paper develops the earlier work and the technique is probably unfamiliar to many involved with conservation, a fuller description of the method is given first.

A. Basic Principles of C-13 FTNMR.

Nuclear magnetic resonance (nmr) spectroscopy depends upon the possession of a magnetic moment by the nuclei of certain isotopes. In a strong magnetic field, a nuclear magnet is permitted to adopt one of only a limited number of orientations with respect to the field direction, and these differ in energy. Thus, in an assembly of like magnetic nuclei in equilibrium with their surroundings, more nuclei will occupy the lower energy state(s) than the higher ones. If electromagnetic radiation of a suitable frequency is input, nuclei in the lower state may be promoted to the higher and a net absorption of energy by the sample occurs; this is the phenomenon of nmr (6).

There is a direct relationship between the strength of the magnetic field and the frequency of radiation required for the nmr experiment: for normal fields from 1-10 Tesla the radiation falls within the VHF radio-frequency range. In principle an nmr spectrum is produced by applying a constant magnetic field to the sample and varying the frequency of the radiation. This experiment is then presented as a plot of absorbed energy against radiation frequency and for an assembly of identical nuclei the nmr spectrum would be a single absorption peak.

In practice the utility of nmr is a consequence of nuclei in normal states of matter being surrounded by electrons which screen them from the influence of the incident magnetic field. This effect is very slight but since electron density and distribution around a nucleus is a function of the bonding environment within a molecule, each distinct environment will in principle give a separate, corresponding absorption peak. This dependence of peak position on the chemical environment of the nucleus in the frequency sweep is the 'chemical shift' and it is

the basis of the power and utility of nmr spectroscopy.

Since the  $^1\text{H}$  isotope of hydrogen, the proton, is the most abundant nucleus, proton-nmr was the first phase of nmr to be developed and this has had a profound influence on organic chemistry over the last two decades through providing subtle new insights into molecular architecture. Unfortunately the chemical shift for the proton is considerably smaller than for larger atoms with more screening electrons. Since most organic molecules are primarily constructed from linked carbon atoms it would be advantageous to observe carbon nmr spectra but the major isotope of carbon ( $\text{C-12}$ ) has no nuclear magnetic moment and  $\text{C-13}$ , which has, is only present in 1% abundance and so gives very weak signals. During the 1970's the development of pulsed Fourier Transform (FT) methods have alleviated this problem and led to the widespread application of  $\text{C-13}$  FTNMR to chemical analysis. The major advantages of FT are:

- i. simultaneous resonance of all target nuclei is stimulated rather than sequential recording of signals. These signals can then be extracted by automatic FT analysis of the resulting response.
- ii. repeated sample stimulation and addition of the digitised responses in a computer memory. This gives relative enhancement of coherent nmr signals in comparison with incoherent signals from electronic background noise.

By such methods  $\text{C-13}$  spectra of good signal-to-noise ratio are typically obtained from about  $10\text{E}3$  acquisitions on samples of about 30 mg run for 3 hours.

$\text{C-13}$  is an extremely delicate probe of chemical structure: the dispersion of signals arising from different chemical environments is up to  $10\text{E}3$  the signal linewidths. Signals are observed in characteristic regions of the spectrum from alkane (saturated  $\text{C-H}$ ), alkene (olefinic, aromatic) and carbonyl (acid, ester, ketone etc) carbons. By convention  $\text{C-13}$  chemical shifts are measured in parts per million (ppm) from the signal of tetramethylsilane (TMS) at 0 ppm which is added as internal reference in the test solution.

$\text{C-13}$  nuclei commonly interact (couple) with other magnetic nuclei, especially protons, in the same molecule which results in signal splitting from chemically distinct nuclei and spectral complications from signal overlap.  $\text{C-13}$  spectra are therefore normally acquired with simultaneous excitation of all protons present with a strong radiofrequency field at the proton frequency. This causes rapid reorientation of the protons and averaging of their interactions with the  $\text{C-13}$  nuclei to zero. This is termed 'spin-decoupling' and is the normal format for  $\text{C-13}$  spectral presentation, as used in the Figures in this paper.

#### B. Experimental

Samples of the seals (30-50 mg) were dispersed in about 0.4 ml of deuteriochloroform and the resulting solution transferred, after filtration of any insoluble residue, to standard 5mm o.d. nmr spinner tubes. The absorption due to the solvent is indicated by 'S' in the Figures. Shellac could only be dissolved satisfactorily with perdeuterodimethyl sulphoxide and this solvent is also indicated by 'S' in figure 1(b).

The spectra were obtained with a Jeol FX100 nmr spectrometer. The FX100 is a pulsed FT spectrometer operating at 25.05 MHz for  $\text{C-13}$  and utilises a 2.35T electromagnet. Samples were excited with an RF pulse of 5 $\mu\text{sec}$  duration (a  $35^\circ$  pulse) and the resulting response (the FID) sampled for 0.7 sec. and 10-30,000 FID's were acquired for each sample.

A spectrum width of 6000 Hz was observed and before FT the summed FID was 'zero-filled' from 8K to 16K data points and weighted with negative exponential and trapezoidal window functions to give a linewidth of about 0.8Hz.

#### C. $\text{C-13}$ nmr Spectra of Waxes and Resins.

##### i. Waxes.

The major structural component of ester waxes is a saturated monoester of long chain carboxylic acids and primary alcohols. Smaller amounts of long chain hydrocarbon, free carboxylic acid and unsaturated species are also present. The mineral or paraffin waxes, however, are predominantly hydrocarbon in nature.  $\text{C-13}$  FTNMR spectra of different waxes are shown in Figure 1 where it is evident that beeswax differs from paraffin wax in the alkane region ca. 65ppm because of the absorption of alkanic

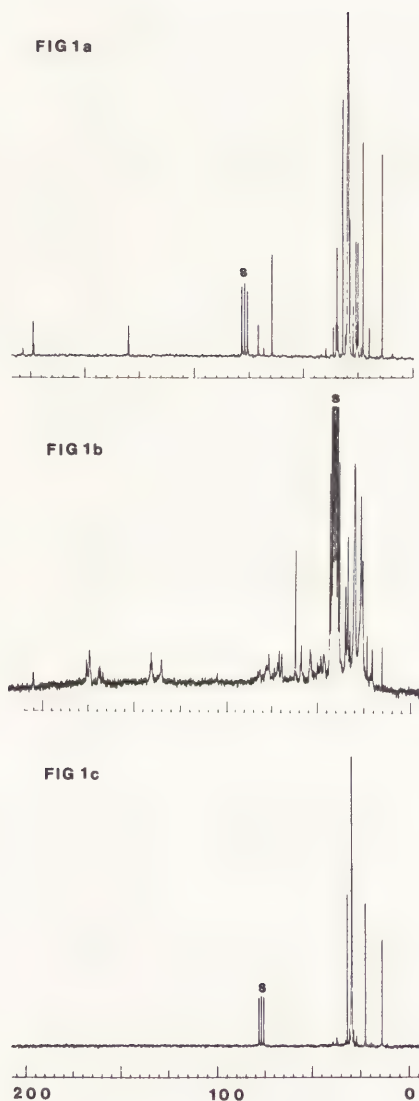


Figure 1.  $\text{C-13}$  FTNMR spectra of waxes: (a) beeswax, (b) shellac, (c) mineral wax. The 29ppm line is characteristic of long chain alkanes and the three waxes can be readily differentiated by absorption in the carbonyl region.



carbons adjacent to ester oxygens common to the former and lacking in the latter. Inspection of Figure 1 also demonstrates that beeswax can be differentiated readily from shellac by features in the alkane, alkene and carboxyl region.

The absorption in the alkenic region of beeswax is indicative of unsaturation and we have previously commented (2) that the loss of this absorption is the only modification of the beeswax spectrum we observe in ancient samples which otherwise seem to retain their chemical integrity.

#### ii. Resins.

Plant resins have terpenoid character and evidence for their composition is largely derived from degradative or separation studies. The major structural units thus identified are the diterpenic acids such as abietic, and the resins are assumed to contain aggregates of such acids.

In identifying resins in the presence of waxes C-13 FTNMR can readily detect the complex cycloalkenyl moieties of the diterpenic acid units in the alkenic regions where wax absorption is minimal. The alkanic region is also fruitful diagnostically because the wealth of carbon environments give distinctive fingerprints easily observed against the background of the simpler wax absorption which is dominated by the CH<sub>2</sub> absorption at 29ppm.

Figure 2 shows C-13 FTNMR spectra of three typical resins, colophony (rosin), copal and dammar. The complexity of these spectra is evident but so is the scope for identification of unknowns through assignments in the alkenic and carbonyl region. Colophony is the resin suspected to be present in early modern seals and we note the three features of its spectrum which single it out from the other resins:

- i. a group of lines around 50ppm (where waxes do not absorb)
- ii. three distinct alkenic groups of lines centred at 145, 135 and 120-5ppm
- iii. a strong carbonyl absorption at 185ppm.

Our primary analytical interest in the resins was in using nmr to fingerprint individual resins and discriminate between them and waxes. Elsewhere we (7) have described other studies of thermally deteriorated resins with C-13 FTNMR and electron spin resonance (esr) spectroscopy, and irradiated resins with esr spectroscopy (8) where the interest has centred around structural studies and in a further C-13 FTNMR study (9, 10) we have pursued the assignment of the complex alkenic region of a variety of different sources of the same resin since we began to identify lines outside the diagnostic alkenic groupings which seemed only related to source. This interesting and potentially useful development in the provenancing of plant resins is further reported in this paper.

iii. Structural Indications from the C-13 FTNMR of Plant Resins. It is possible to make some observations on the spectral features of the resins identified in this study and comment on their possible structure. Most noteworthy is the alkenyl feature which is far more complex than the cycloalkenyl structure of abietic and related acids suggests. This may indicate an aggregated or polymeric cycloalkenyl structure with many non-equivalent cycloalkenyl or quasi-aromatic carbon atoms. This tentative conclusion is supported by the esr study (7) which showed the presence of very stable 'intrinsic' free radicals in the resins which may well be stabilised by an extended quasi-aromatic structure. Interestingly, this stability was no greater in amber or fossil Kauri resin (8) than in fresh modern resins, indicating that it was indeed an intrinsic feature of the resin molecular architecture, and not one due only to polymerisation or decay.

#### C-13 FTNMR of Historical Non-Metallic Seals

A range of mediaeval and early modern Royal and Great Seals, detailed in the Table, were sampled as described and the C-13 FTNMR spectra obtained.

##### i. Mediaeval Seals.

All the mediaeval seals showed the beeswax spectrum with no indication of resin. The only difference between these spectra and that of modern beeswax is in the expected loss of the unsaturation lines in the seal samples, but we note that this is not accompanied by any comparable increase in carbonyl species which suggests that this is not due to oxidation or hydrolysis. Careful examination of the spectra of the mediaeval seals,

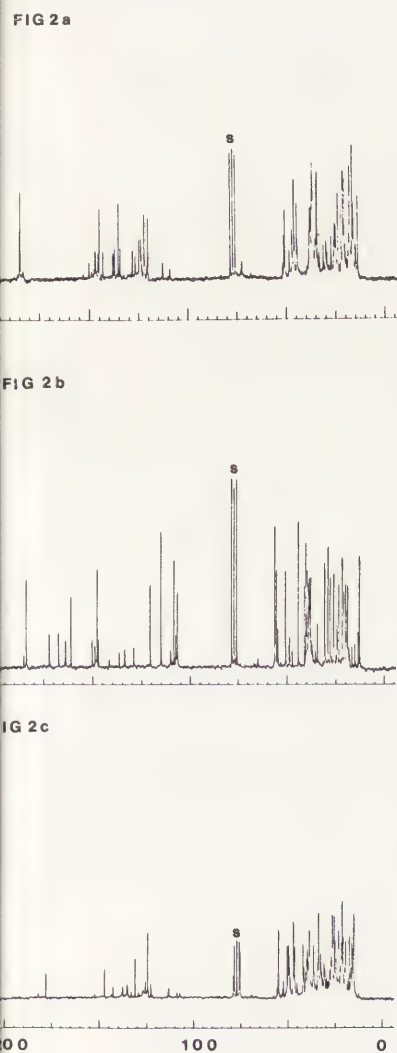


Figure 2. C-13 FTNMR spectra of plant resins: (a) colophony, (b) copal, (c) dammar. The complex lines in the alkene region (120-150ppm) provide detailed structural information and also allow fingerprinting of the resins. The three alkenyl line groups in colophony are characteristic of all sources of this resin.

however, demonstrated that only in the oldest (Kings John and Stephen) had the unsaturation lines disappeared and that with younger samples the unsaturation lines were progressively stronger, indicating that loss of unsaturation occurs only gradually after a considerable period. This point will be developed in a further report.

This survival may well be due to the anhydrous nature of the wax and we therefore suggest that the bloom discerned on these surfaces is not microbial but associated with a physical change such as a slow crystallisation of the wax through the loss of small amounts of volatiles.

#### ii. Early Modern Seals.

All these extracts show complex spectra indicative of wax and resin components. The spectrum shown in Figure 3 demonstrates this complexity and at the same time illustrates how the major resin and wax features indicated in Figures 1 and 2 can be identified in the presence of each other. Thus the strong  $-CH_2-$  hydrocarbon chain feature at 29ppm identifies the major alkane component of wax and the other lines, indicated in the specimen wax spectra in Figure 1, show how ester and hydrocarbon waxes can be differentiated by the lines around 60ppm diagnostic of  $-CH-$  adjacent to the ester carbonyl which is absent in mineral wax. Inspection of the Table shows that some of the George III seals contain mineral wax on this basis, indicated by the absence of characteristic wax ester carbonyl at 175 ppm. We further note that some of the William IV and Victoria seals contain an ester wax which has not yet been positively identified.

The resin component in all these seals is clearly demonstrated as colophony from the three characteristic groupings of cycloalkenyl lines in the 100-150ppm region mentioned above and the carboxyl absorption around 185ppm. Closer examination of the spectra, however, revealed that within this overall pattern differences were discernable both within the group and in comparison with our standard colophony (Figure 2(a)). The alkenyl absorption regions for a number of the seals are shown in Figure 4 where the seal colophony is provisionally classified and grouped in terms of its complexity relative the standard colophony in Figure 1.

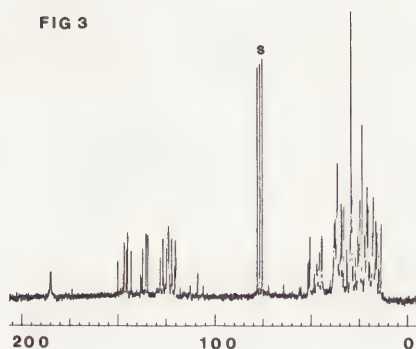


Figure 3. C-13 FTNMR spectrum of the Great Seal of Queen Victoria showing the presence of beeswax and colophony.

The variation in resin C-13 FTNMR spectra around the basic skeletal pattern has previously been noted by us in a study of other resins, especially copal (9), and suggested as a function of source rather than physical state, and one inference from this study of the Royal Seals is that perhaps the colophony categories identified actually correspond to provenance of the resins. It is impossible to give an unequivocal answer on this before an extended study of a wide range of individual colophony sources has been made, but we note that the similarities in the carbonyl and alkane regions among the spectra of the resins and the persistence of the cycloalkenyl fingerprint suggests that these differences are more likely to be due to source variations than deterioration due to oxidation or other mechanisms: in support of this inference we also note that the integrity of the wax spectrum is preserved and the absence of new carbonyl and carboxy lines suggests that oxidation has not occurred.

#### Conclusions

A study of a wide range of historical non-metallic seals with C-13 FTNMR confirms our earlier report that mediaeval seals only contained beeswax as the organic component and that none of these seals showed any sign of chemical deterioration. This observation confirmed the opinion already expressed by us that changes in the appearance of the seals were caused by physical rather than chemical changes.

In the early modern seals all were found to contain both wax and a resin, and whereas the resin was exclusively colophony, the wax differed in nature between the reigns, with beeswax being supplanted by mineral wax in the reign of George III, and this in turn being supplanted by another wax ester, probably not shellac, in succeeding reigns, although several of the William IV and Victoria Seals were also noted to contain beeswax. Inspection of the colophony spectra did not suggest that any oxidation or deterioration of the resin had taken place but differences in the spectra allowed a tentative categorization which supported earlier conclusions that differences in the sources of the colophony were being detected.



## Acknowledgements

We thank Glaxo Group Research for the use of instrumental facilities and the Keeper of the Public Record Office, Dr G. Martin, for permission to sample their collection of non-metallic seals.

TABLE OF SEALS ANALYSED AND THEIR ORGANIC COMPONENTS

SEAL	Components	
1. Mediaeval Seals		
King John (1199-1216), Great Seal	Beeswax	
King Stephen (1135-1154), Great Seal	Beeswax	
Edward II (1307-1327), Great Seal	Beeswax	
Edward III (1327-1377), 2nd Great Seal	Beeswax	
James II of Scotland (1449), Great Seal	Beeswax	
Edward VI (1547-1553), Great Seal	Beeswax	
2. Early Modern Seals		
	Wax	Colophony
George I (1714-1727), Great Seal of 1718	Beeswax	III
George II (1727-1760), Great Seal of 1729	Beeswax	II
George III (1738-1829), 1st Great Seal Ref R17.7	Mineral Wax	I
Royal Seal Ref R26.1	Mineral Wax	II
Great Seal, Ref R29.4	Mineral Wax	I
4th Great Seal (1805) Ref H04/1	Non-ester wax*	I
Great Seal Ref F9	Beeswax	III
Great Seal, Ref R24/4	Beeswax	III
George IV (1820-1830), Great Seal Ref C2767	Ester wax	II
William IV (1830-1837), Great Seal Ref R19.9	Ester wax*	I
Great Seal Ref R25.5	Ester wax*	II
Victoria (1837-1901), Great Seal, 1837 Ref R18.8	Ester was	II
Palatine of Lancaster Ref R27.2	Beeswax	III
Later Great Seal Ref R30.5	Beeswax	I

## Notes:

\* indicates the presence of some beeswax.

The term ester wax excludes beeswax, tallow and shellac.

Non ester wax indicates a similarity to paraffin wax but with differences so far not explained.

The distinction between colophony I, II and III is illustrated in Figure 4.

## BIBLIOGRAPHY

1. Guide to Seals in the Public Record Office. Public Record Office Handbook 1, 2nd Edition, HMSO, London, 1968.
2. Cassar, M., Robins, G.V., Alstin, A., and Fletton, R.A., Organic Components in Historical Non-Metallic Seals Identified with C-13 Nuclear Magnetic Resonance Spectroscopy, *Nature* 1983, 303, 238-239.
3. Dobbie, J.J. and Fox, J.J., The Composition of Some Mediaeval Wax Seals, *Transactions of the Chemical Society*, 1914, 105, 795-800.
4. Tothill, R., *The Art of Limning*, Reprinted by the Society of Scribes and Illustrators, London 1979, from the original published in London, 1573.
5. Cassar, M., *The Conservation and Technology of Non-Metallic Seals*, University of London Institute of Archaeology, unpublished undergraduate thesis, 1982.
6. F.W. Wehrli and T. Wirthlin, *Interpretation of C-13 NMR Spectra*, Heydon and Sons, London 1976.
7. Robins, G.V., Sales, K.D., Fletton, R.A., and Convert, J., Polymers in Archaeology: Information on Degraded Organic Materials from Magnetic Resonance Techniques, *Polymer* 85, Royal Australian Chemical Society, 1985, Melbourne, 325-327.
8. Robins, G.V., Sales, K.D., and Oduwole, D., Electron Trapping in Plant Resins: an Assessment of ESR Dating Possibilities, *Ionics*, Tokyo, 1986, 435-438.

FIG 4a

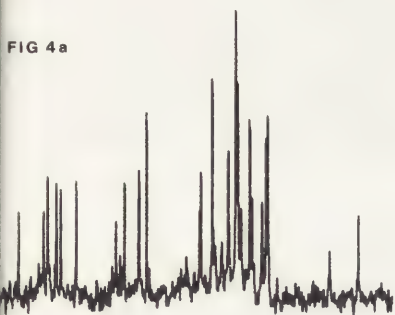


FIG 4b

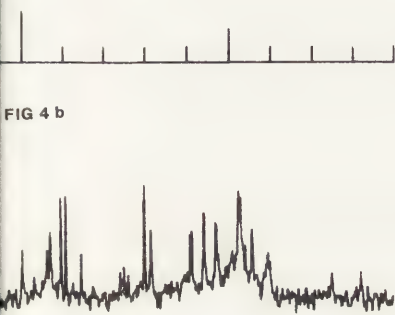


FIG 4c

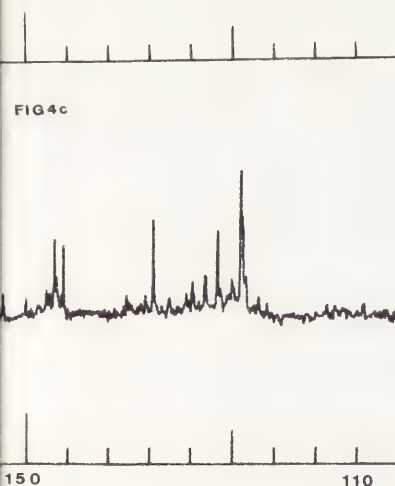


Figure 4. C-13 FTNMR spectra of the alkenic region of some early modern royal seals showing the three categories of colophony fingerprint observed.

- a) Colophony I: The Great Seal of William IV Ref R19.9
- b) Colophony II: George III Royal Seal, Ref 26.1
- c) Colophony III: Victoria, Later Great Seal, Ref R30.5.

9. Robins, G.V., Pendlebury, D., Fletton, R.A., and Elliott, J., The application of C-13 NMR in the Analysis of Art Objects and Archaeological Artefacts, in Proceedings of the 5th Seminar on the Applications of Science in the Examination of Works of Art Museum of Fine Art, Boston, USA, in press.
10. Robins, G.V., The Assessment of the deterioration of Resinous and Related Varnish Materials with C-13 Fourier Transform Nuclear Magnetic Resonance (FTNMR) Spectroscopy, Proceedings of the 1st International Conference on Non-Destructive testing in Conservation of Works of Art, ATTI, Rome, 1983, Vi/9.1 - 9.



## SUMMARY

A 3-D laser scanner system developed by the National Research Council of Canada and implemented by Hymarc Engineering Ltd. as the YSCAN-60 is described. The scanner provides the museum field with an accurate, high-speed and non-contact method of capturing three-dimensional surface data from objects for basic documentation and research and for the fabrication of replicas or supports for objects of complex shape using numerically controlled (NC) machining. The operation and design of the laser scanner are described. Applications of the system to a range of artifacts and natural science specimens having varying colour, texture and reflectivity were tested. The system has applications in the recording of living subjects including the human face for the purpose of fabricating mannequins for display. Interpretation of the range data is facilitated by the use of an interactive graphics system which also provides various editing functions. An integral part of the system is a software package which generates the co-ordinates to drive an NC milling machine and an accurate replica of a North Pacific Coast stone mask was produced in this way.

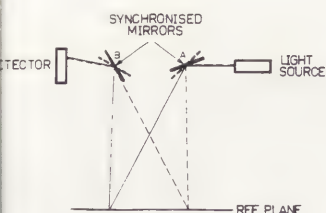


Figure 1a

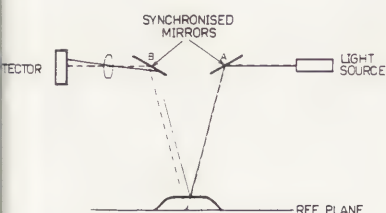


Figure 1b

## APPLICATIONS OF A LASER SCANNER TO THE RECORDING AND REPLICATION OF MUSEUM OBJECTS

J.M. Taylor and I.N.M. Wainwright  
Analytical Research Services, Canadian Conservation Institute  
Ottawa, Ontario, K1A 0M8, Canada

F.R. Livingstone  
Hymarc Engineering Ltd.  
P.O. Box 5127, Station F, Ottawa, Ontario, K2C 3H4, Canada

M. Rioux and P. Boulanger  
Division of Electrical Engineering, National Research Council of Canada  
Ottawa, Ontario, K1A 0R8, Canada

Introduction

In recent years there have been a number of new developments in the field of machine vision using laser scanners to remotely capture three-dimensional surface data from objects. The Canadian Conservation Institute is currently working with the National Research Council of Canada and Hymarc Engineering Ltd. to explore the feasibility of using such a laser scanner in museum documentation and conservation, and in the recording and measurement of artifacts and natural science specimens.

The creation of geometric databases for computer aided (CAD) design is frequently the most complex aspect of computer based design and analysis systems. In the case of objects having a regular geometry it is practical to generate a geometric model analytically. However there are many applications where there is a need to create a database by extracting dimensional information from an object of complex shape. (Boulanger *et al.*, n.d.). Examples may be found in the areas of medicine (prostheses, plastic surgery, *etc.*) and in the measurement of castings (*e.g.* ships' propellers).

In the museum field a number of potential applications of such systems can be identified:

- basic measurement of three dimensional artifacts and specimens for documentation and research purposes.
- assessment of the accuracy of replicas (*e.g.* a cast bronze replica)
- comparison of the shape of an object at different periods of time, for example before and after conservation treatment, before and after a loan for exhibition, or to investigate weathering, deterioration, or dimensional change over time.
- generation of digital data and contour plots which can be used either with manual or numerically controlled (NC) milling machines to fabricate replicas (at any scale), display mannequins, or supports for objects of complex shape.

The accurate measurement of three-dimensional objects is very time-consuming. Depending upon object size and the degree of accuracy required, hand measurement, stereophotogrammetry or coordinate measuring machines are used. Developments in machine vision in recent years have added another technology that is capable of recording measurements in three dimensions with a speed and accuracy which lend themselves to many applications in museums. An important aspect of this new technology is that it offers a non-contact form of measurement, a critical factor in dealing with many artifacts and specimens.

Laser Scanning Systems

This paper describes prototype systems implemented at the National Research Council of Canada and at Hymarc Engineering Ltd. Through a PILP (Program for Industry Laboratory Projects) technology transfer project with the National Research Council of Canada, Hymarc Engineering Ltd. has designed, built and tested a 3-D laser scanner which consists of a novel laser-ranging camera and an interactive graphics system for the editing and visualization of object data. These systems have been described elsewhere in detail by Rioux (1984), Livingstone and Rioux (1986) and Boulanger *et al.* (n.d.) from which the following brief summary is drawn.

The basic system consists of a laser light source, a scanning mechanism to project the light onto the surface of an object, and a position sensor with a collecting lens looking off-axis for the reflected light spot. The system uses the well established approach of triangulation to measure distance. This is done by a straight forward application of trigonometry to the geometric relationship between the angle of the scanning beam and the position of the reflected beam on the surface of the position sensing detector.

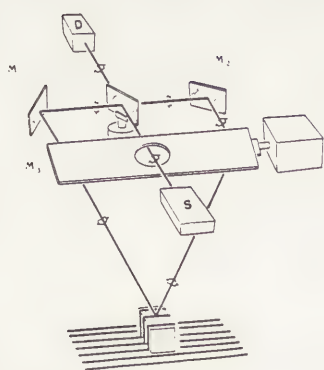


Figure 2a

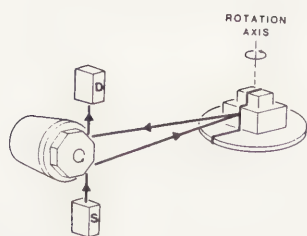
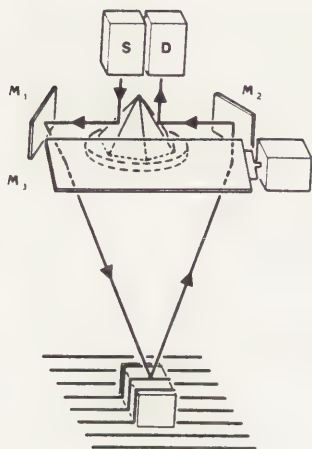


Figure 2c

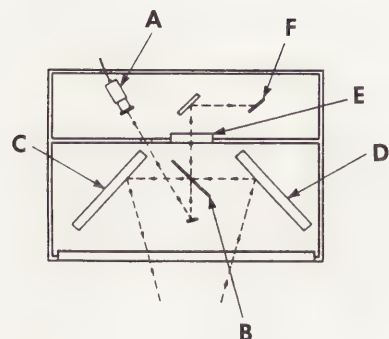


Figure 3a

The unique feature of the system, however, is the use of synchronized scanning which enables a large field of view to be attained without compromising accuracy. The concept is illustrated in Figure 1a. A light source, in this case a laser, projects a beam via a mirror A onto a reference plane. The reflected light is captured by a second mirror B and reflected onto a detector. By rotating mirror A a scan is made of the reference plane. Synchronizing mirror B with mirror A has the effect of keeping the light spot on the detector stationary. Autosynchronization between the two scanning mirrors is obtained by using either pyramidal mirrors or a plane mirror coated on both sides. One facet is used to project the light beam and another facet is used for detection.

Introducing a lens into the system as shown in Figure 1b converts the system into a camera with a depth of field in which measurements can be made. Placing an object on the reference plane causes a deflection of the spot on the detector; this deflection is related to the height of the object above the reference plane. Thus measurement in the Z-axis is independent of the scan width. By increasing the focal length of the lens, the depth of field of the camera is reduced and the accuracy is increased.

There are several methods of generating the scan in the orthogonal direction. The raster mode (Figure 2a) consists of a rectangular raster scan which is equivalent to a view from a camera at a fixed position pointing at the object, producing surface data in the form  $z(x,y)$ . For applications where speed is important (e.g. the digitizing of a human face), a fast scanning unit that incorporates a pyramidal mirror consisting of six facets is used (Figure 2b). In another mode, a vertical scan is performed in a fixed plane and the object is rotated on a turntable resulting in an array of data that describes the object for  $360^\circ$  around a cylindrical axis. (Figure 2c).

#### HYSCAN-60 Laser Scanner

The HYSCAN-60 camera used for the tests (Figure 3a) was configured for the specific application of measuring large marine propellers. The requirements were a field of view of 60 cm, a depth of field of 50 cm and an accuracy of  $\pm 0.25$  mm. These requirements set the geometry of the optics and therefore the dimensions of the camera which are 264 mm x 190 mm x 90 mm. For the present tests, the field of view was reduced to 20 cm which was sufficient to test the application. A helium-neon laser is connected to the camera by a fibre optic cable and the laser beam is focused by the lens A. A double-sided mirror B driven by a galvanometer performs the scanning. The laser beam from the galvanometer mirror is directed onto the object by the left-hand mirror C and the right-hand mirror D collects the information back from the object. It is next transmitted to the scanning mirror B and then focused by a second lens E onto a position sensor F. This detector is a 1024 element CCD linear array. The intensity of the spot is also acquired by the system permitting an intensity image to be displayed along with the 3-D image.

The HYSCAN-60 camera records measurements in the X-direction and the Z-direction (depth). To obtain the Y-direction data, the camera or the object has to be moved. Hymarc Engineering Ltd. constructed a test assembly which consists of a 1.2 x 1.2 metre vibration isolation table on which is mounted a gantry with a carriage driven by a stepping motor (Figure 3b). The camera can be moved either over the table top or at  $90^\circ$ , so that objects that are too large for the table can be scanned. The control of the camera and the robot, the acquisition of the data and its processing, are carried out by the system microprocessor and the host computer, an IBM PC AT. The system arrangement is shown in Figure 4.

The system can be programmed to vary the number of data points measured on a given object. The number of points per line can be varied from 128 to 2048. Line spacing can be as little as .01 mm. A high density scan is required where an object is very detailed. Another adjustment on the system is the integration time on the detector. If an object does not return much light, then the integration time can be increased to obtain a better image. An increase in scanning density or integration time results in an increased time for scanning the object.



The objects tested included:

- a pair of pantaloons from the archaeological site of a Basque whaling station on Saddle Island, Red Bay, Labrador; fabrication of supports for delicate archaeological textiles; evaluation of capability to capture textile contours and detail.
- a severely corroded cruciform artifact found at Ferryland near St. John's, Newfoundland; recording of fragile artifacts prior to conservation treatment
- a sample of waterlogged wood; dark, wet surface; applications in the measurement of dimensional change in wood during water removal.
- a specimen of fulgurite, a fragile tube of silica glass formed by lightning striking sand; to explore applications in the fabrication of display mounts for delicate objects and specimens of complex shape.
- a mammoth ( *mammuthus* ) tibia and molar; measurement and recording of palaeontology specimens for purposes of replication, study and exchange of information between museums.
- a preserved toad ( *Bufo americanus* ); measurement and recording of live zoological specimens such as fish, amphibians and reptiles.
- a human face to evaluate applications in fabricating mannequins for museum displays.
- a number of replicas of typical ethnographic artifacts including two coppers; a bone and abalone sole catcher; a wood and metal fish club; a bone and argillite scraper; a stone mortar; a number of small ivory or bone figurines which are difficult to record by conventional means.
- examples of historical ceramics and fragments; recording, matching and reconstruction with the possibility in future of using the data for pattern recognition studies.

- a marble bust; application of cylindrical scanning about 360°; white reflective surface.
- a North Pacific Coast wooden mask
- a replica of a North Pacific Coast (Tsimshian) stone mask; recording, comparison with similar masks and replication for exchange.
- a carved North Pacific Coast pole which once stood at Kitwanga.

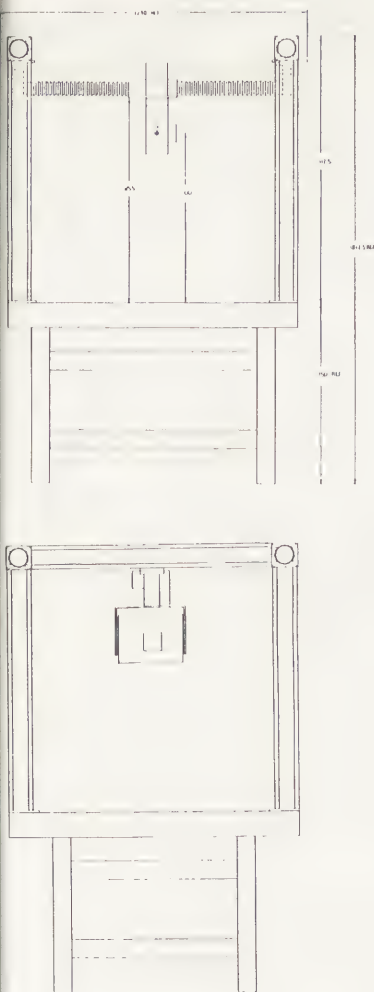


Figure 3b

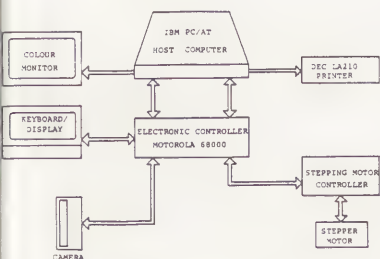


Figure 4

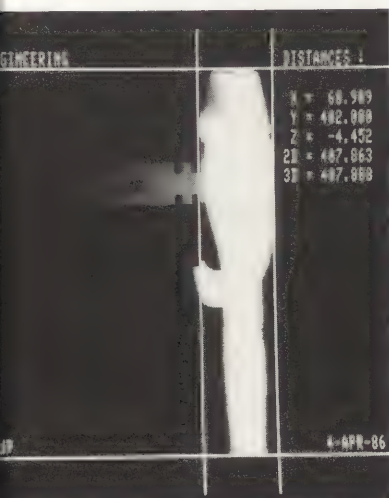


Figure 5

#### Software - The Editor

This study has successfully demonstrated that it is now possible to capture several million bytes of data representing the surface of an object such as a mask in a matter of a few minutes. The spatial resolution can be varied depending upon the density of points sampled by the scanning system;  $\pm 0.25$  mm is a typical value. Once in computer memory, the data can be edited and selected for display and manipulation using graphics software.

The output of the **HYSCAN** system is a set of X,Y, and Z coordinates describing the scanned object. A graphics display system of the National Research Council of Canada was used for this pilot project. Image data was output on floppy disks from the **IBM PC AT** and input to NRC's **VAX** system. Graphics software, some developed by NRC, was used to display the images of the objects using the scanned data as input.

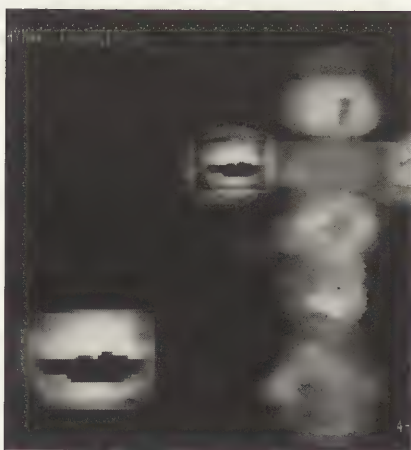


Figure 6a



Figure 6b

Black-and-white photographs were taken from the display screen of the VAX computer. The Z, or depth, information is represented by 64 levels of gray scale, white being closest to the viewer, black farthest away and the intervening space coded in shades of gray. **Figure 5** illustrates the ability to make measurements in three dimensions on the object using the cursors on the computer display screen. The measurements displayed represent the distances in X, Y and Z between the points marked by the lower left hand crossing of the cursors and the upper right hand crossing of the cursors. Thus, X gives the width, Y gives the height, Z the depth, 2-D gives the length of the projection on the X-Y plane, and 3-D gives the same diagonal length taking into account the Z information. All data are in mm except Y which is in cm. **Figure 6** illustrates two other features of the display: the zoom capability to look more closely at a selected area (**6a**) and the ability to display a profile (**6b**).

Due to the number and variety of objects to be scanned, it was agreed that a raster scan would be sufficient to determine if any particular group of objects presented problems for measurement. In a raster scan, the object is placed on the gantry table and the camera passed over it. This results in Z-dimensions being measured from a view point above the object. If the object has surfaces at, or close to,  $90^\circ$  to the camera plane, then, as can be appreciated, the laser spot does not scan them (shadow effect) and information is not returned. To obtain an image of all surfaces, the object either has to be rotated or multiple views obtained and merged. Two objects, the marble bust and a replica of the Tsimshian stone mask, were rotated to illustrate the concept. The mask was rotated through  $180^\circ$  in steps of  $0.9^\circ$  and the image so created is shown plotted out in **Figure 7**. This is equivalent to unfolding the mask and laying it out flat.

An interactive graphics system, based on an Adage/Ikonas RDS3000 display, provides a number of ways of rendering the data, as well as providing various editing functions which are necessary to compensate for some of the shortcomings in the scanning process. Interpretation of range data is facilitated by the use of isometric and wire mesh displays and by the use of shaded images. **Figure 8** shows other ways in which the data obtained from the stone mask can be represented.

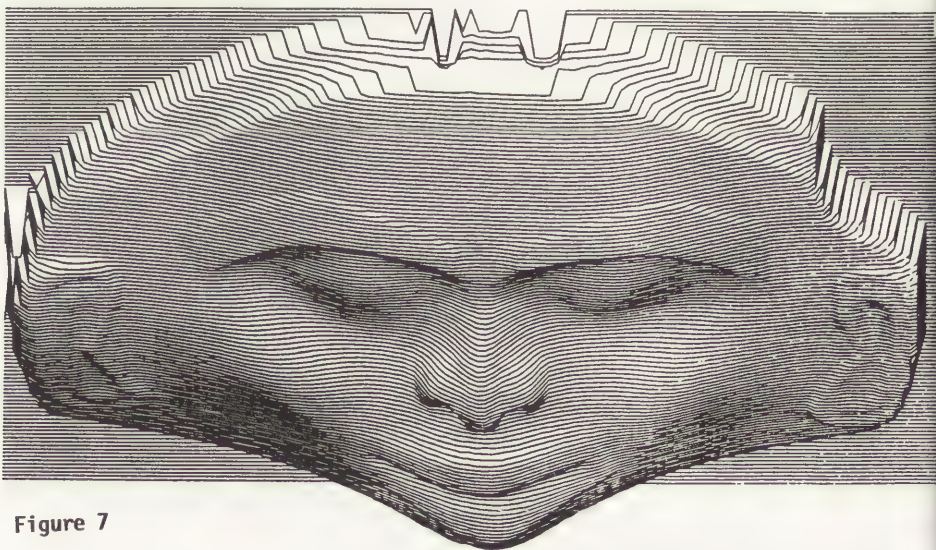


Figure 7





### Numerical Control (NC) Milling - Replication of Objects

After a satisfactory object representation has been achieved in the editor, the resulting data can be passed to a machining program that will produce the tool path for a multi-axis milling machine. A program called POLYHEDRAL NC, based on one that was first developed by J.P. Duncan at the University of British Columbia, is used. Polyhedral machining divides the surface into polyhedra and calculates the position of a spherically ended cutting tool by touching the many faces of the polyhedron without interference or undercutting. (Boulanger et al., n.d.)

One of the immediate aims of this feasibility study was to demonstrate that a detailed model could be made of a complex surface such as a mask using numerically controlled machining. Figure 9 illustrates a foam replica made of a Tsimshian stone mask by the Manufacturing Technology Centre of the National Research Council of Canada using data obtained by the laser scanner. Replication of scanned objects in a variety of materials is possible depending upon specific requirements. The saving in time over conventional methods of replication, and the fact that the method is completely harmless to the object, offer tremendous benefits to the museum field.

### Conclusions

Although the tests conducted must be regarded as preliminary, the project to date has demonstrated that a laser scanner has wide potential application in conservation, museum registration and replication. Its speed could greatly facilitate the basic recording of large quantities of three-dimensional objects. If some sacrifice of spatial resolution can be tolerated to increase speed, it is also possible to record living specimens using the method. The scanner used a 10 mW helium neon laser, operating in the low energy, red end of the visible spectrum, which passes instantaneously over any given point on the artifact surface. It can therefore be regarded as harmless with respect to photochemical degradation. Appropriate precautions must be taken to protect the eyes of living subjects. This laser source gave acceptable results for a wide range of materials of varying colour, texture and reflectivity.

This technology has great potential in many areas of museology and conservation. Not least of these will be the ability to replicate objects for which traditional moulding methods are unsafe. Another potentially very useful application for conservation is in the manufacture of display and storage supports for fragile objects of complex shape.

### Acknowledgements

The authors wish to thank the following individuals for their contribution, interest and support of the project and for providing suitable objects for evaluating the laser scanner: James Tuck, Memorial University of Newfoundland; George MacDonald, Brian Arthur, Kitty Bishop-Glover, Jean-Pierre Chrestien, James Donnelly, Canadian Museum of Civilization; Don McAllister, Francis Cook, Rob Waller, Gerry Fitzgerald, Charles Gruchy, National Museum of Natural Sciences; Ken Macleod, Judy Logan, David Grattan, Wilf Bokman, Jeremy Powell, Canadian Conservation Institute; Mark Thomas, Alexanderu Tulai, Bruno Alie, Hymarc Engineering Limited; Jacques Domey, Luc Cournoyer, National Research Council of Canada.

### References

- Boulanger, P., Evans, K.B., Rioux, M. and Ruhlmann, L. Object Input for CAD/CAM Using a 3D Laser Scanner, NRCC No. 25446. Ottawa: National Research Council of Canada (n.d.) : 7 pp.
- Hymarc Engineering Ltd. Report on a Test Program to Investigate the Measurement of Museum Artifacts by a 3-D Laser Scanner, unpublished report, 8 May 1986.
- Livingstone, F.R. and Rioux, M. "Development of a Large Field of View 3-D Vision System," SPIE Proceedings, no. 665 (June 1986) : 188-194.
- Rioux, M. "Laser Range Finder Based on Synchronized Scanners," Applied Optics, 23(1984) : 3837-3844.



Figure 9





## SUMMARY

## X-RAY COMPUTER TOMOGRAPHY (XCT) IN WOOD CONSERVATION

to begin with the basic principles of X-ray computer tomography (XCT) are elucidated, considering the need for a more comprehensive application of modern natural scientific methods of investigation in wood conservation. Next, the different ways of obtaining revealing information by this procedure concerning the object and its conservation are discussed. As an example of the demonstration of the efficiency of XCT, the consolidation of a baroque picture frame with methyl methacrylate is described. The relevant chapter contains information concerning conservation technique and CT interpretation of the different phases of treatment. This contribution concludes with research which the authors consider to be necessary with a view to attaining the full scope of application of XCT for wooden objects.

Achim Unger and Jens Perleberg  
Central Restoration Workshops  
Berlin State Museums  
Bodestrasse 1/3  
Berlin  
DDR-1020  
GDR

What is the purpose of XCT?

Testing methods not causing damage of wooden objects are only applied in few cases. Such methods are, for instance, oscillation measuring and conventional X-ray photos for the recognition of active infestation by wood-damaging insects and to prove the effectiveness of relevant control measures /4/. Since adequate guarantees of the success of treatment cannot be given without precise condition analysis of an object before and after conservation, appropriate methods of investigation need to be sought.

Technological novelties in other branches of science must be carefully watched and, wherever possible, these should be utilized to solve one's own problems. During recent years the scope of diagnostic procedures in medicine has been considerably extended by the introduction of XCT. This method also opens up new ways in the field of conservation /2, 9/, e. g. for wood.

What is XCT?

As in conventional X-ray photography technique, XCT is also a pictorial procedure. The weakening of the X-rays taking place during the penetration of an object, however, is primarily measured in CT by detectors, in contrast to the otherwise customary photographic reproduction /10/. With the aid of a computer the individual weakening values can be converted into scanning elements (pixel) with corresponding gray values, which are arranged in a scanning field (matrix) into a graded gray value picture. This picture appears on a screen. A further quantitative analysis is facilitated by means of digital saving the picture on floppy discs.

The actual advantage of CT over conventional X-ray methods results from the changed recording technique. In conventional techniques the object, or certain parts of it, are irradiated in their entire space volume. The computer tomograph can X-ray the object in layers. This does not involve heterodyning shadows by other layers and details are much clearer distinct. For the irradiation in layers, an X-ray tube is fixed to a gantry of the tomograph, and opposite it several hundred detectors, which revolve around the object during the investigation (fig. 1). The object lies in the gantry opening, at right angles to the fan-shaped rays emanating from the revolving X-ray tube. In order to obtain a cut-image as far as possible free of heterodyning shadows, the object has to be irradiated from at least 360 (better 720) angles. The layer density (2...10 mm) is determined by the degree of concentration of the X-rays. The entire scanning process is completed within a few seconds.

What can XCT accomplish?

The stationary CT- apparatus, so far developed for medical diagnosis, is in principle also suited for the examination of transportable wooden "patients". The scale ranges from unmounted and mounted wooden sculptures, gun and rifle shafts, parts of picture frames or of furniture from the museum, to samples of detached construction wood from protected monuments, and smaller waterlogged wood findings in archaeological excavations. Gantry openings and the size of the CT-room determine the dimensions up to which wooden objects can be examined.

Under the effect of X-rays, sculptures reveal the secrets of their inner life. Cavities consciously made by the sculptor and metallic connecting elements, not seen from the outside, become visible. A work of art, which appears to the superficial viewer as carved out of a piece of wood, suddenly reveals its structure out of several components of different sorts of wood. Glued joints clearly stand out in the X-ray picture. The same applies in regard to colour mounting. Pigments produced with the use of

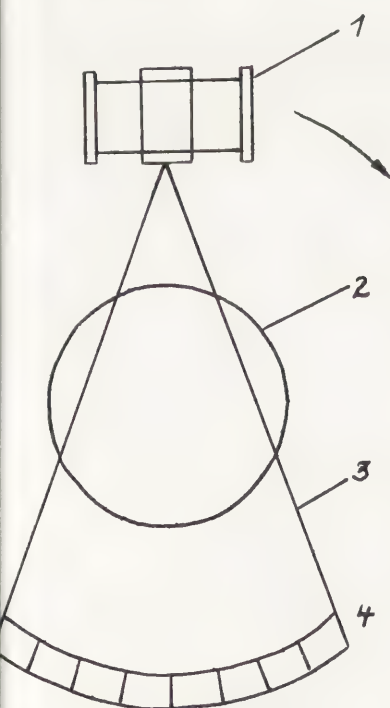


Fig. 1: Principle scheme of XCT. 1 X-ray tube, 2 object, 3 fan-shaped ray, 4 detectors

elements of high atomic numbers are marked particularly clearly.

XCT-photos are most valuable in assessing the "health condition" of wooden art objects. The whole extent of damage caused by wood-destroying insects or fungi in wooden objects outwardly appearing stable can be established. Passages eaten into the wood by larvae of wood-destroying beetles, termites and the insects themselves are shown in the CT-picture. The places of their destructive activity and the position of the cause of the damage, changing in time, can be ascertained with precision. This again offers opportunities for testing the effectiveness of pest combat measures, for instance by physical methods /1, 18/ or gassing /16, 17, 19, 20/. Insects and fungi, which destroy wood, alter the specific gravity of the wood.

In waterlogged wood of shipwrecks, pile foundations and from primeval and early historic excavation sites, aerobic and anaerobic decomposition processes, depending on the situation of the finds, impaired the specific gravity of the formerly healthy wood. Since healthy and diseased wood weaken X-rays to a different degree, important data on the material decomposition which prevails at present in old wood can be obtained.

In future, it may be assumed, it will become possible to undertake a control of the load-bearing capacity of certain accessible wooden construction parts of roof framing or exposed pile foundations on the spot. This forecast is based on the fact, that work has already been started in the development of transportable CT-apparatus with hinged gantry /3/. Valuable museum exhibits would then be able to remain in their permanent place when examined, which would avoid transportation damage.

The CT-analysis, which avoids destructive effects on wooden objects, ultimately provides the wood restorer with a concrete idea of the extent of the damage to be dealt with and allows him to apply corresponding conservation methods far more systematically than hitherto. This applies in regard to the treatment of the material with wood conservation and consolidating agents. A CT-documentation of the most important parts of the object of conservation, before, during and after treatment, allows the restorer to control the effectiveness of his measures immediately.

In most cases, the conservation agent contrasts sufficiently to the structure of the wood. However, suitable contrasting substances may be added to conservation agents, which will make further details visible. CT-photos taken in the course of the conservation of an object with a certain agent will allow future generations of wood restorers to establish the durability of conservation and possible negative modifications. For this purpose it is only required, that the same centre of investigation should take renewed CT-photos. Thus cracks caused by inadequate durability of consolidating agents or inappropriate air conditioning may be recognised at an early stage and corresponding measures can be taken in good time.

Finally it should be pointed out, that XCT can also render valuable services in the dendro-chronological dating of cultural objects of wood. Early and late wood weaken X-rays to a different degree. This can be clearly seen in CT-photos. In this way each annual ring may be clearly distinguished. Independent evaluation units, belonging to the installations of XCT-work places, can measure the gravity of the wood to X-rays in radial direction and express it in terms of a weakening value curve. This curve reflects the sequence of annual rings in every detail. The weakening value curve of the object to be dated then needs to be synchronised with the corresponding curves of the wooden objects forming the respective chronology, in order to ascertain their exact age.

#### Which results are available at this stage?

During the years 1983/84 two life-size wooden sculptures of Christ on the cross from the sculpture collection of the State Museums in Berlin were for the first time subjected to a CT-analysis on the initiative of the Director of the Central Restoration Workshops of the State Museums in Berlin, Mr. G. Jacob. The CT-photos produced the evidence to prove, that one of the Christ-sculptures had movable limbs, and that the object in question was a procession-crucifix /3/.

These investigations were followed by the CT-analysis of a



conservation process of particular interest. The focal point of the operation were measures of consolidation to protect wooden objects against damage from insects and/or fungi.

A wide range of consolidating agents are available for the treatment of dry wood (humidity rate  $u < 30\%$ ) and damp wood (humidity rate  $u > 30\%$ ) /11, 15/. For smaller and medium-size wooden museum exhibits, acrylic and methacrylic compounds are applied primarily to stabilize the material. These compounds are mainly applied in two forms:

- a) as polymers in a solvent,
- b) as monomers, pure, without a solvent.

Unmounted cultural objects made of wood, badly damaged by insects and/or fungi are suited to complete impregnation with monomer acrylic and methacrylic compounds. In this field good results have been obtained in the consolidation of gun and rifle shafts /14/ and of wooden construction parts of a gun mounting /5, 6, 13/ with methyl methacrylate (MMA). The MMA is polymerised in the wood by way of thermocatalytic or radiation-chemical methods /12/.

To extend the scope of application of MMA, the problem had to be solved, whether after a full impregnation of wooden objects with this substance and its subsequent hardening new mounting was possible. For this purpose a baroque frame of lime wood, badly damaged by insects, reinforced by a supporting frame of pinewood was selected, which was to be newly gilded after MMA treatment. Preliminary experiments proved that this way could be taken /7/.

Subsequently the four sides of the frame, of about 1 m in length each, (original and support frame) were soaked in MMA in a tub, under normal pressure and at room temperature. 1 % 2,2'-azo-bis-isobutyronitril in relation to the MMA quantity was used as a catalyser. As a result of the advanced degree of destruction the sides of the frame had absorbed the required quantity of the solution within one hour.

The polymerisation of the MMA within the wood took place according to a procedure already described above /5/ with the aid of warmth covers at an average temperature of 60 °C. As a rule the MMA hardens within the wood after about 20 hours. In order to avoid a homopolymerisation on the surface of the wood, each side of the frame was placed in a wire box specifically made for this purpose, which was covered with foil for the hardening process.

Dependant on the degree of destruction of the parts of the original frame, the absorbed quantity of MMA was 30...50 % in relation to the initial mass of lime wood.

Fig. 2 shows the pre-mounted sides of the baroque frame on a working scaffold after consolidation with MMA.

Fig. 2: Frame after consolidation of the sides with MMA and preliminary assembly photo: J. Perleberg)

The CT-analysis undertaken on the example of a frame-side before, during and after MMA stabilisation was to give information about the structure of the frame, the behaviour under impregnation of the original and the support frame, the distribution of the MMA after impregnation and consolidation, and to give indications of possible negative modifications in the object as a result of the heat exposure in the course of polymerisation.

The CT-photos were produced under the direction of Dr. sc. med. J. Planitzer, Deputy Director of the Neurological Clinic of the Charité, Berlin and head of the department of Computer Tomography, with the aid of a "Somatom SF" implement made by Siemens & Co., (FRG).

The conditions of recording were: tension: 125 kV, energy dose - 230 mAs, layer density- 8 mm, scanning time- 10 s. These data corresponded to those of skull examinations. The further densitometrical evaluation of the CT-pictures took place in the separate "Evaluscop" evaluation unit, with the use of floppy discs. The "Evaluscop" allows the quantitative evaluation of axial sections according to the density of the material under exposure to X-rays. Weakening value curves on one pixel-line (approx. 1 mm), or selectively, on several pixel-lines ("secondary sectional image") can be obtained. Furthermore, so-called "regions of interest", may be measured.

Fig. 3a shows a cross-section of the left side of the frame presented in fig. 2, in the condition prior to treatment. It can be recognised that the part in this area is composed of three

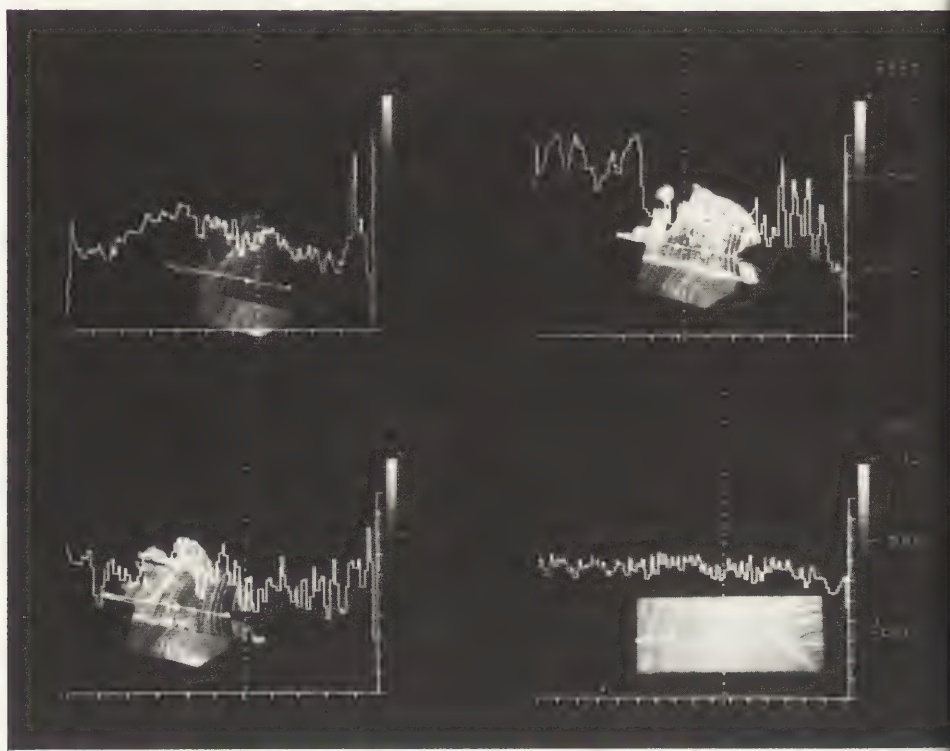


Fig. 3: CT sections across a frame side and native lime wood (from top left to bottom right)  
 a) untreated side; b) impregnated side; c) consolidated side;  
 d) healthy, recent lime wood (photo: Charité, Berlin-GDR)

elements. The original frame on top consists of two parts, between which the partly damaged glue joint is visible. The connection between the original and the lower supporting frame, on the other hand, is still intact. The light scale perceptible on the edge of the picture shows the weakening of the X-rays in Hounsfield-units. Dense, still intact parts of the wood greatly weaken the X-rays and appear as light areas in the picture. Dark areas indicate damaged wood. Passages eaten into the wood by insects, open glue joints, etc.

Fig. 3a shows that the original frame resists to X-rays far less than the supporting frame. The particularly dark right half indicates serious damage. The light area in the lower section of the support frame, also seen in fig. 3c, is caused by a technically conditioned reflection. The weakening value curve blended into fig. 3a represents a measure of the gravity of the material along the slightly curved line running along the cross section from left to right. In the middle of the original frame, therefore, a relatively high gravity still prevails. The marked rise of the weakening value curve on the right is caused by a remnant of the original gilt priming.

For a comparison of the various phases of conservation with one another, the position of the section, recording parameters and contrast focusing must be kept constant. This requirement was mainly complied with. Only in fig. 3b, which shows the frame side impregnated with MMA, the intersectional position slightly deviates from the settings of the pictures in fig. 3a and 3c.

The MMA, as shown by the increasing lightness, is exclusively contained in the original parts of the impregnated element. The evidently damaged outer parts are well impregnated. The weakening value curve confirms this condition, at the same time proving the lesser impregnation of the rather better preserved core area. The consolidated original part (fig. 3c) shows a reduced gravity (see fig. 3b), which, however, is still considerably greater than in the untreated wood (see fig. 3a). The cause is estimated to be the inadequate MMA retention capacity of the badly damaged areas which particularly emphasises the evaporation losses in the course of its exposure to heat.

Looking at the weakening value curves in fig. 3b and 3c, the



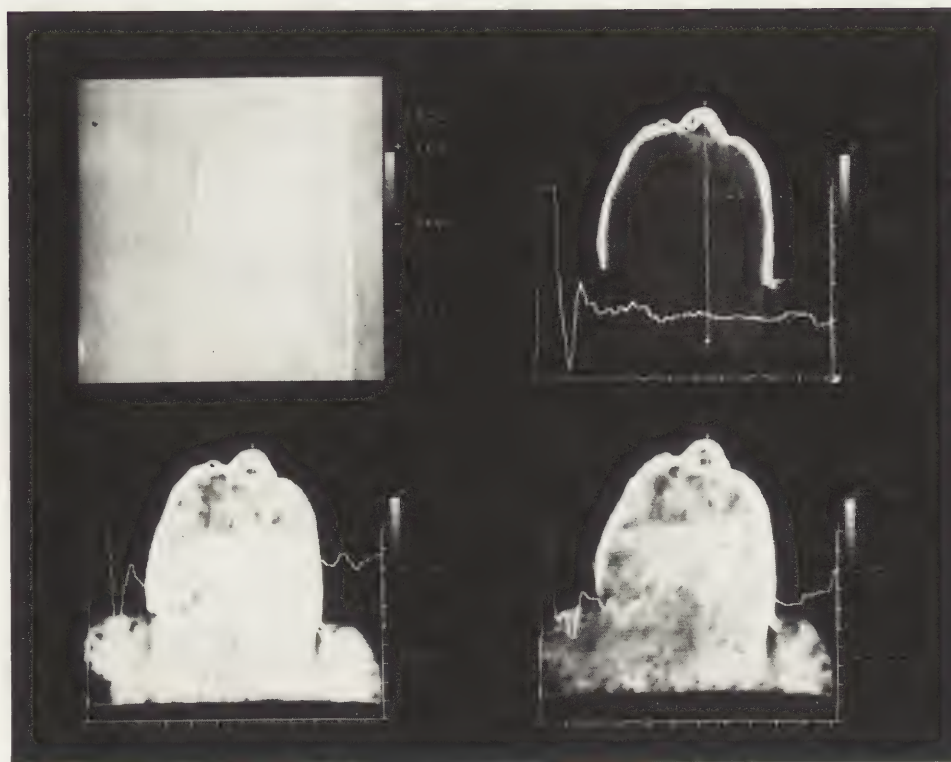


Fig. 4: CT-photos of the mounted head of a cherub (from top left to bottom right):

a) topogram; b) before impregnation; c) after impregnation; d) after consolidation

Consolidation agent: MMA (photo: Charité, Berlin-GDR)

positive fact is noted, that the gravity of the material is far more homogeneous in the consolidated frame part. In a first comparison it is even close to the gravity of the native lime wood shown in fig. 3d. The weakening value curve in the native wood was not ascertained precisely along the cross section, in order to ensure that the weakening value curves of fig. 3c and 3d should coincide as closely as possible in relation to the investigated area. The recording of a weakening value curve in radial direction would be appropriate, for example, for dendro-chronological investigations. Nevertheless fig. 3d indicates the course of weakening value curves in dendro-chronological studies.

Generally speaking, the results so far described allow the conclusion, that the phases of conservation processes can be adequately observed and interpreted by means of XCT. Experiences collected in connection with other objects, e.g. the sculpture of an angel's head (fig. 4) confirm this statement. Relevant details will be published separately /8/.

#### What remains to be done?

The quantitative densitometrical evaluation of CT-pictures of wooden objects by the presentation of variable weakening value curves or the measuring of "regions of interest" to begin with only reflects the weakening of X-rays depending on the material. The density of the material, exposed to X-rays is not tantamount to physical density in  $\text{g/cm}^3$  in the case of wood with the specific gravity. Weakening of X-rays and specific gravity however, are in relation to each other. This relationship must be ascertained.

The following method can be used to this effect: with the aid of norm testing elements with defined humidity rate, calibration curves are made of healthy wood and of wood destroyed by insects, for example, concerning the dependency between the weakening of X-rays in Hounsfield-units (HU) and the specific gravity of the wood. Fig. 5 shows a calibration curve of this kind for native lime wood.

If a wood restorer is faced with the task of conserving a sculp-

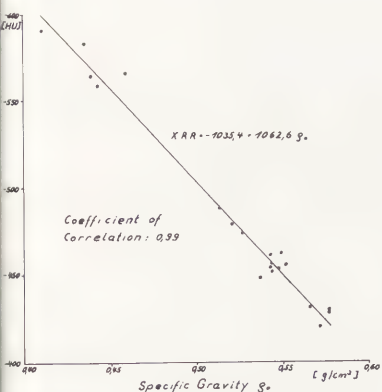


Fig. 5: Dependence of the weakening of X-rays on the specific gravity in oven-dry, recent lime wood.

ture badly damaged by insects, CT-pictures are made of the main areas of damage and the weakening of X-rays in the "regions of interest" is measured. The mean values in HU are used for reading off the remaining specific gravity with the use of the calibration curve for the insect-damaged wood. By comparison with the specific gravity of the healthy wood, the approximate loss in specific gravity can be ascertained. That loss in specific gravity for its part is an indicator of the quantity of consolidating agent to be applied to the wood.

CT-photos taken after stabilisation serve to check whether the specific gravity of the healthy wood has been restored. Since there are also connections between the specific gravity and the strength properties of the wood, links between the X-ray weakening and the strength properties of healthy and damaged wood can be established, either by way of the specific gravity, or directly, with the aid of stability testers. Thus the remaining strength parameters of art objects can be ascertained and compared with those of the healthy wood, without causing any damage. With reference to these data the quantity of conservation agent essential for achieving an adequate measure of stability may be calculated. This allows for a systematic treatment of the object concerned, based on measuring values, instead of applying a more or less empirical conservation procedure.

It should be noted, however, that the research work necessary for the establishment of the calibration curves for the most important kinds of wood can presumably be undertaken only at larger museum laboratories, in cooperation with wood research institutes. It would be advisable in this connection to optimize still further the recording parameters hitherto obtained for CT-pictures with reference to wood, as the material of specific interest.

#### Bibliography

- /1/ Bär, M.; Kerner, G.; Köhler, W.; and Unger, W. "Die Bekämpfung holzerstörender Insekten mit ionisierender Strahlung." Neue Museumskunde 26(1983): 208-215.
- /2/ Bashmakova, L.I. "An approach of tomography." Paper delivered at the Fourth Triennial Meeting of the International Council of Museums Committee for Conservation, 1975, in Venedig.
- /3/ Jakob, G.; Ehlich, V.; Unger, A.; and Perleberg, J.: "Anwendungsmöglichkeiten der Röntgen-Computertomographie auf dem Holz- und Kunstsektor." Holztechnologie 27(1986): 85-88.
- /4/ Kerner, G.; Thiele, H.; and Unger, W. "Gesicherte und zerstörungsfreie Ortung der Larven holzerstörender Insekten im Holz." Holztechnologie 21(1980): 131-137.
- /5/ Lachmann, M.; Nissel, D.; Peters, M.; Reichelt, L.; and Unger, A. "Die Konservierung der Holzbauteile der 'Faulen Magd'." Neue Museumskunde 29(1986): 292-298.
- /6/ Nissel, D.; and Unger, A. "Zu Stand und Ergebnissen der Konservierung von Holzbauteilen an der Lafette des Stabringgeschützes 'Faule Magd'." Paper delivered at the Fifth International Restorer Seminar, 9 July 1985, in Veszprem.
- /7/ Perleberg, J.; and Unger, A. "Zum Problem der Neuvergoldung von mit Methylmethacrylat konsolidierten Kunstobjekten aus Holz." Neue Museumskunde 28(1985): 277-278.
- /8/ Planitzer, J.; Unger, A.; and Perleberg, J. "Kontrolle der Konservierung von Kulturgut mittels Computertomographie." Neue Museumskunde 30(1987).
- /9/ Reimers, P.; and Riederer, J. "The examination of art by means of X-ray computer-tomography (GAT)." Paper delivered at the Seventh Triennial Meeting of the International Council of Museums Committee for Conservation, 1984, in Copenhagen.
- /10/ Seidel, K. "2. Computertomographie." In Bildgebende Diagnostik abdominaler Erkrankungen, edited by M. Lünig and G. Liess, Leipzig: Georg Thieme Verlag, 1986.
- /11/ Unger, A. Holzkonservierung Schutz und Festigung von Kulturgut aus Holz. Leipzig: Fachbuchverlag, planned publication 1988.



- /12/ Unger, A.; Reichelt, L.; Bär, M.; Reinhardt, J.; and Nissel, D. "Erfahrungen bei der strahlenchemischen Konservierung von Holz mit Methylmethacrylat." Neue Museumskunde 25(1982): 202-206.
- /13/ Unger, A.; Reichelt, L.; Lachmann, M.; Nissel, D.; and Peters, M. "Zur Verfestigung der hölzernen Lafette der 'Faulen Magd' mit Methylmethacrylat." Holztechnologie 25(1984): 242-243.
- /14/ Unger, A.; Reichelt, L.; and Nissel, D. "Zur Konservierung von Holz mit organischen Verbindungen. Verfestigung alter Pistolenschäfte mit Plasten." Neue Museumskunde 24(1981): 58-65.
- /15/ Unger, A.; Reichelt, L.; and Nissel, D. "Zur Konservierung von Holz mit organischen Verbindungen. Entwicklung und Möglichkeiten." Neue Museumskunde 24(1981): 118-128.
- /16/ Unger, A.; and Unger, W. "Begasungsmittel zur Insektenbekämpfung in hölzernem Kulturgut." Holztechnologie 27(1986): 232-236.
- /17/ Unger, W. "Die Begasung der denkmalgeschützten Fischerkirche in Ferch (Kreis Potsdam-Land) mit Blausäure." Holztechnologie 24(1983): 241-244.
- /18/ Unger, W. "Möglichkeiten zur Bekämpfung holzerstörender Insekten durch physikalische Methoden." Holztechnologie 25(1984): 264-269.
- /19/ Unger, W.; Bischoff, J.; and Fielitz, L. "Zum Einsatz von Phosphorwasserstoff gegen holzerstörende Insekten in denkmalgeschützten Gebäuden." Holztechnologie 25(1984): 229-232.
- /20/ Unger, W.; Bischoff, J.; and Fielitz, L. "Zur Bekämpfung holzerstörender Insekten mit Phosphorwasserstoff." Neue Museumskunde 28(1985): 140-141.





## SUMMARY

Since the development of infrared reflectography for the study of paintings, the working document, the infrared reflectogram assembly, has been produced by an arduous and painstaking process. Individual sequential images of a painting's underdrawing are photographed from a monitor screen in overlapping segments which, when developed and printed must be sliced together to create a photo montage of the complete image selected. An additional complication accompanying this process is the uneven tonal quality of individual prints. The many variables introduced into the method of achieving the reflectogram assembly, not the least of which is the relative manual dexterity of the workers employed, often combine to produce a less than perfect image, sometimes even one whose distortion and tonal problems result in illegible and useless document. Stom printing can lessen the tonal disparities, but is costly and there is currently no way around the cut-and-paste method assembly.

To address this problem, that is, the time-consuming and not entirely accurate *modus operandi* of infrared reflectogram assemblies, the Metropolitan Museum of Art initiated a project in collaboration with the National Gallery of Art and the Amparo Corporation to by-pass the photographic method of recording the underdrawing of a painting, intending to achieve the desired result through computer programming. The outcome of this effort, which brought together the expertise of an art historian, physical scientist, paintings conservator and two computer scientists, is now ready for presentation and critical discussion.

The current state of the art computer system is described that provides the requisite computational capabilities in a very compact portable package. Such portability should significantly assist in the collection of data from various sources other than from the user's institution.

## ASSEMBLY OF INFRA-RED REFLECTOGRAMS BY DIGITAL PROCESSING USING A PORTABLE DATA COLLECTING SYSTEM

George Wecksung, Randell Evans and James Walker  
Amparo Corporation  
P.O. Box 2687  
Santa Fe, New Mexico 87504 USA

Maryan Ainsworth and John Brealey  
Metropolitan Museum of Art  
New York, New York 10028 USA

Gary W. Cariveau  
National Gallery of Art  
Washington, DC 20565 USA

The infrared reflectogram assembly currently employed for studying paintings presents many difficulties that seriously interfere with the detailed analysis of such paintings. In particular, the inability to geometrically register the images precisely and the inability to match their brightness levels correctly seriously flaw such work. Additionally, the unavoidable presence of film edges, to which the human eye is especially sensitive, detracts significantly from the value of this technique as presently conducted. Figure 1 is an example of an infrared assembly constructed by photographic techniques that clearly demonstrates the problems cited. For these reasons and others, personnel from the Metropolitan Museum of Art, the National Gallery of Art and the Amparo Corporation initiated a program to construct infrared mosaics by digital techniques. We can now report that this program has been successfully completed and we present today a discussion of this work and demonstrate our results.



Fig. 1: Infra-red reflectogram assembly produced by usual photographic techniques

The task of constructing an IR reflectogram mosaic digitally involves performing three basic tasks, namely:

1. Data Collection
2. Correcting Camera Distortions
3. Digital Processing

Let us consider the first of these tasks, i.e. data collection. It is essential that the data collecting procedure be conducted in a highly controlled manner. The need to overlap adjacent images in order to correlate similar features in them is a requirement of the digital procedure as it is with the photographic technique and should be performed in a consistent and uniform manner. Economy of data collecting calls for minimizing image overlap but such overlap must permit the identification of sufficient numbers of similar features for good registration. We have found 20% overlap to be quite adequate. The layout of the grid of picture taking should be given careful consideration. In this regard, such things as camera-image separation, resolution requirements, rigidity of camera or image motions, etc., must be tightly controlled.

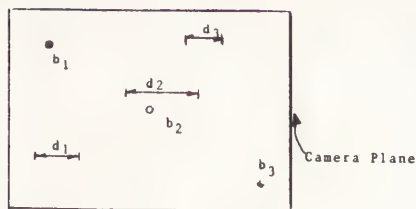


Fig. 2: Illustration of camera distortion

Additionally, of paramount importance is the need to have as uniform an illumination of the picture as possible.

Turning to Task 2, we note that all mosaics constructed by photographic techniques will suffer from the very serious difficulties associated with camera distortions since it is almost impossible to correct for them photographically. The distortions referred to are geometrical distortions and light level or brightness distortions. Simplistically, geometrical distortion is the fact that a given distance or separation in the image will be mapped into different distances or separations in the camera plane depending on where it appears in the camera plane. Similarly, brightness distortion is when a given brightness of some point in the image appears with different brightnesses in the camera plane depending on where the point appears in the camera plane. These distortions are illustrated in Figure 2. The fixed distance  $d$  in the image plane maps into different distances  $d$  depending on where it appears in the camera plane. Similarly the given brightness  $b$  in the image plane maps into different brightness levels  $b$  depending on its location. One can correct for such distortions digitally if they are not pathological as is the situation with most high quality vidicon cameras. To do this one employs calibration procedures involving the imaging of targets with precisely controlled geometrical and brightness level values. These calibration procedures are a basic requirement that must be employed if one really desires high quality results. The outputs from the calibration effort are correction functions which are applied to all the images forming the mosaic and which remove the camera distortion from these images and permit highly improved geometrical registration and brightness level matching.

We now turn our attention to the actual mosaic construction by digital processing. Instead of signals from the I.R. Vidicon appearing on a monitor as an image which is then photographed, they are sent to an analog to digital converter resident in a micro computer such as an IBM XT or AT. This digital image can alternatively be played back from the computer through the digitizer going digital to analog, and be viewed on a T.V. monitor. As stored in the computer an image is an array of numbers with the value of the number being a measure of its brightness and its position in the array corresponding to its position in the image. For compatibility with U.S. television standards our arrays are 512 points called pixels along a horizontal line by 480 such lines. Each pixel is characterized by eight so-called bits which permit 256 different brightness levels. We point out that the average human eye can only distinguish about 40 brightness levels.

Once all of the calibration images and the images comprising the painting are digitized and stored in the machine, the following tasks are carried out:

- a. The picture images are corrected for camera distortion using the calibration functions;
- b. Corresponding points are read between pairs of overlapping images to register such images relative to each other
- c. The images are tested for brightness level matching in the overlap area and are adjusted as required.
- d. The registered and brightness level corrected images are formatted to fit into a mosaic framework and written out on floppy disks.
- e. Such disks are then read onto a nine-track digital tape which is sent to a facility that can use such tapes to drive an optical imaging device. The output from this device is a digital negative.
- f. The digital negative is processed photographically to produce an enlarged print.

Though we have given a rather simplistic version of the actual processes involved, it should serve to indicate the major steps involved.



In Figure 3 we present an infrared reflectogram assembly produced by the digital processor called Mosart. We submit that it represents a considerable improvement both visually and technically.



Fig 3: Computer constructed infra-red reflectogram assembly

This assembly of 100 images presently would require about 3 days of operator time to produce. This includes the data collection time but does not include the time associated with sending the data out for print production at a digital imaging facility.

Through the above work was performed on Amparo Corporation's standard IBM-AT computer, future work at the Metropolitan Museum will be performed on a system especially configured for both at home and in the field data collection. It consists of an IBM-AT clone called a Touch-I in which resides a 60 Megabyte Streaming Tape Unit, a regular high density floppy disk drive and an Imaging Technology PC-Vision Board. This is augmented with a stand along 70 Megabyte hard disk. The hard disk will be resident at the Museum and will not be employed for data acquisition or processing elsewhere. Instead, the 60 Megabyte streaming tape will be used as the in-field storage device. This results in a package weighing roughly 22 pounds. On returning to the Metropolitan, collected data will be copied onto the hard disk from the tape for further processing as required.

A block diagram of this system is shown in Figure 4.

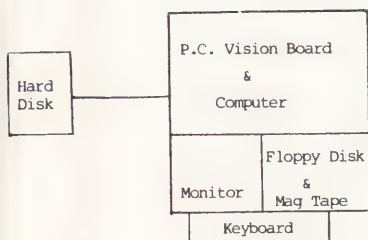


Fig. 4: System Block Diagram





## SUMMARY

A few organic colorants are found on East Asian paintings; the situation regarding the identification of most of them is unsatisfactory. At the Freer Gallery of Art we are seeking to extend our past work on the identification of inorganic pigments into this area. The present report discusses the practicality of thin-layer chromatography (TLC) as applied to the rather simple case of gamboge. TLC seems capable of distinguishing gamboge constituents from most other yellow organic natural products, but the sensitivity of the method is not as good as might be wished. It appears, nevertheless, to have some practical application in this area.

## ORGANIC COLORS IN EAST ASIAN PAINTINGS: THE IDENTIFICATION OF GAMBOGE

John Winter  
Conservation Scientist  
Freer Gallery of Art  
Washington, DC 20560 USA

Introduction

The majority of pigments found in East Asian paintings are inorganic, and quite often derived from minerals (1, 2). However, a limited number of organic colors have been reported, with varying degrees of success attending their identification. The main ones noted, mostly from the Japanese area, have been the following.

## 1. Indigo

This appears to be the most firmly established, and a number of identifications, mostly made on the basis of specific chemical reactions, have been published (1,3).

## 2. Gamboge

Use of this yellow gum-resin as a pigment in East Asian paintings is believed from historical evidence, to go back at least to the 8th century (1, 4). The problem is that only rarely has experimental evidence been presented to support the attribution as gamboge. Quite often, indeed, a study has gone no further than asserting the presence of an "organic yellow"; it is true that, in this context, gamboge seems the most probable of available candidates. The problem is pursued further below.

## 3. Organic Reds

Several authors have noted the presence of organic reds on Japanese paintings (1, 3); there is also some evidence for a similar colorant in the Chinese field (5, 6), but in nearly all cases no attempt at identification was made. Nor is it clear whether only one material is involved. Taguchi and Taguchi (7) did produce reflectance spectrophotometric evidence for anthraquinone pigments of the type of carminic or laccaic acids in the case of a 17th-century Japanese painting. The presence of a sample of stick lac in the 8th-century collection of the Shōsōin in Nara, Japan (8) suggests that lac dye may have been available for painters, but at present the whole question remains unresolved.

## 4. Organic Brown

This has cropped up several times (3, 9, 10), and possible similarity to Vandyke brown has been suggested (3, 10) but essentially it remains uncharacterized.

## 5. Purples and Violets

Violet and purple colors sometimes occur and the importance of such a hue in Japanese art history has been discussed (11). In many cases mixtures of a red and a blue pigment are used (the latter sometimes being indigo). The dye from sappan wood (brazilein) has also been suggested as an organic purple (1, 7), but again uncertainties remain. Sometimes, purple dyes may have been used to color the supports (12), rather than to manufacture a pigment as such.

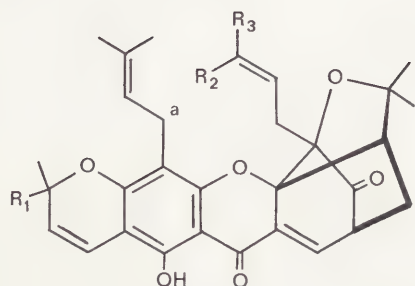
Identification of organic colorants in the context of East Asian paintings is subject to severe constraints. The surface density of such a colorant on the painting is typically very low, so that a sample that can be reasonably obtained (where sampling is permitted at all) is usually very small. This leads to a requirement for great sensitivity, and consequently also for stringent control of contamination effects, or "bad blanks". The alternative approach is the "non-destructive" one of producing a reflectance spectrum from a small area of the painting itself. This may also encounter problems from low surface density of the colorant, particularly for infrared spectroscopy. Visible reflectance spectra were produced, to excellent effect, from a 17th-century Japanese handscroll by the Taguchis (7), and by R. L. Feller and his coworkers (13) from Edo-period Japanese color prints. The latter are rather different from paintings in the materials they use, and make more extensive use of organic colors, but in both areas such approaches as these could well be exploited further.

For the time being, we have mainly looked at the question of how far the technique of thin-layer chromatography (TLC) can be applied to organic color identification in this field. In the first place, the specific case of gamboge has been used to explore the limits of sensitivity and specificity for the technique. This approach has the virtue of simplicity, among others; it also has

drawbacks, as will be seen. It is not, of course, new, and abuts on the use of TLC for the identification of dyestuffs on the one hand (14) and resins on the other (15). No doubt it can with advantage be supplemented by other methods, and may perhaps be superseded by them.

### Gamboge

Gamboge is a yellow gum-resin produced by various trees of the genus *Garcinia* growing in south and southeast Asia. The resinous portion (soluble in organic solvents such as ethanol) forms the major component and is responsible for the yellow color.



- I Gambogic acid:  $R_1 = (CH_2)_2CH(CH_3)$   
 $R_2/R_3 = CH_3/CO_2H$   
 II Morellin:  $R_1 = R_3 = CH_3$ ,  $R_2 = CHO$   
 III Morellic acid:  $R_1 = R_3 = CH_3$ ,  
 $R_2 = CO_2H$   
 IV Isomorellic acid:  $R_1 = R_2 = CH_3$ ,  
 $R_3 = CO_2H$   
 V Morellinol:  $R_1 = R_3 = CH_3$ ,  
 $R_2 = CH_2OH$   
 VI Desoxymorellin:  $R_1 = R_2 = R_3 = CH_3$

In addition to its use in East Asian paintings, gamboge has been commercially available in Europe since at least the early 17th-century (16), where it has not only been used by the water-color painter, but is also found as a varnish colorant in many recipes for varnishing metals and other substrates (17). Hooker's green, a mixture of gamboge with (usually) Prussian blue, was also sold as an artists' pigment in the 19th century (18), but in modern times gamboge appears to have fallen out of use in most of these areas in the West.

The constituents of the yellow resinous portion of gamboge may vary somewhat with the source, but are all of the structural type shown here (I - VI). "Siam gamboge" of European commerce has generally had gambogic acid (I) as the major constituent (19) but Venkataraman and other Indian chemists (20) have found morellin (II) in *Garcinia* species from India, together with minor constituents such as III - VI. The chromophore is seen to be the same in all these compounds, and the presence of structures of this unusual hydroxanthone type (which does not appear to have been reported from plants of genera other than *Garcinia*) may be taken as diagnostic for some version or other of gamboge. In other words, looking for gamboge comes down to looking for one or more compounds of this structural type.

### Identification Methods

No one technique is a panacea. Gamboge has been used for a number of different purposes, and, even within the confines of East Asian paintings, different methods, or a combination of methods, may at times be appropriate for its study. This report does not deal with all available techniques in detail, but some of them may be summarized as follows.

#### 1. Microscopy

Gamboge is a transparent yellow, of amorphous, resinous appearance under the microscope. With caustic alkali solution it turns orange: this change occurs because a phenolic group attached to the chromophore in structures I - VI is converted to the phenolate anion giving a change in visible absorption and hence in color. The test is thus not very specific, since phenolic groups are often found in yellow natural products.

#### 2. Spectroscopic Methods

The ultraviolet-visible absorption spectrum of gambogic acid and its congeners seems to be quite characteristic, comprising about four peaks of fairly high extinction coefficient (19). A published identification (7) made use of the visible and near-UV part of the spectrum in the reflectance mode, taking in the highest-wavelength peak at ca 360 nm. The UV-visible spectrum would appear to afford a practical identification method, as the high intensity of the absorption both discriminates against many possible interferences and reduces the sample size needed to produce a transmission spectrum.

The infrared spectrum is characteristic, but the author is aware of no identifications based on it. The widespread availability of Fourier transform techniques and the development of various reflectance methods makes this a more practical possibility than hitherto, but infrared spectroscopy continues to have the drawback that mixtures of substances (and gamboge can usually be expected to occur in conjunction with other materials) give an ill-defined "envelope" spectrum that is often extremely difficult to interpret. Similar remarks apply to mass spectrometry, and many spectroscopic techniques may turn out to be most useful when "hyphenated" to a separation method.

#### 3. Separation Methods

High performance liquid chromatography (HPLC) has obvious potential, though we still await published application to gamboge. The preparation of sufficiently volatile derivatives of the gambogic acid group of products should enable gas chromatography



to be used, with the possibility of coupling to a mass spectrometer; again, we are aware of no gamboge identifications by this well-known method. There remains thin-layer chromatography.

#### Thin-layer Chromatography (TLC)

TLC has of course been a common laboratory technique of wide application for many years. The concern here was to investigate two aspects before applying it to the routine checking of removed samples for gamboge. One was the specificity, or the ability to distinguish gamboge from other materials that might be present. The other is the sensitivity, or the ability to identify gamboge in amounts sufficiently small to be useful for our purposes.

##### 1. Specificity

TLC offers two characteristics for distinguishing between different substances: the rate of migration along the plate (the Rf value), and the way in which the spots react to reagents applied to the plate. For this work, precoated silica gel analytical plates (on glass), purchased from a laboratory supply company, were used. The results reported are from development with cyclohexane:ethyl acetate:acetic acid (50:50:1); a mixture in which the cyclohexane was replaced with petroleum ether (b.p. 60-90°) behaved similarly except that the Rf values appeared to be less reproducible. Visualization methods are dealt with below.

Our sample of gamboge (purchased in Japan ca 1970) gave a main spot (Rf 0.63-0.65) moving at the same rate as gambogic acid (applied as the pyridine complex (19)), together with three (sometimes four) less intense spots trailing the first and also reacting as phenols (see below). Most of the yellow natural products checked were widely separated from the main gamboge spot; some of them are listed in Table 1. The only compound found so far staying close to gambogic acid is the flavonoid chrysin (5,7-dihydroxyflavone) with an Rf under these conditions of 0.60. Chrysin, a pale yellow color, is not so far known as a colorant in the East Asian area, and an experiment demonstrated that it is resolved from the main gamboge spot under our conditions.

TABLE 1

Rf values of some yellow natural products  
(conditions as in text)

<u>Product</u>	<u>Rf</u>	<u>Notes</u>
Gamboge	0.64, 0.52, 0.42, 0.35	Absorbs UV; phenolic
Chrysin	0.60	Absorbs UV; phenolic
Morin	0.10	UV-fluorescent; phenolic
Curcumin	0.40	UV-fluorescent (strong); phenolic
Quercetin	0.28	UV-fluorescent (weak); phenolic
Catechin	0.09	Absorbs UV; phenolic
Crocetin	0.40	Non-phenolic; difficult to detect
Berberine	Does not migrate	UV-fluorescent (strong); non-phenolic

Since gamboge has also been used as a varnish colorant, some plates were run with samples of common natural varnish resins as well as gamboge, viz. damar, mastic, copal, shellac, rosin, and dragon's blood. All except the last of these gave a complex series of spots, none of which were very close to the main gamboge spot (dragon's blood appeared to be very slow moving under these conditions, with a measured Rf of 0.02). However, resin constituents such as those dealt with here are also readily distinguishable from gamboge constituents by reactions with spray reagents as is seen below.

It was found advantageous to use the self-fluorescent type of silica gel TLC plate for this work. These incorporate an inorganic phosphor that fluoresces bright yellow under short-wave ultraviolet radiation (wavelength 254 nm). The gamboge spots in Table 1 (and most of the other compounds listed there) quench this fluorescence, i.e. they show up dark against the fluorescent background. Since the plates do not fluoresce under long-wave UV, fluorescence stimulated by the latter or reagents that depend upon such fluorescence, can still be used, the spots having first been located under short-wave UV.

The following spray reagents were checked for possible utility in

distinguishing gamboge from other materials.

a. Ferric Chloride

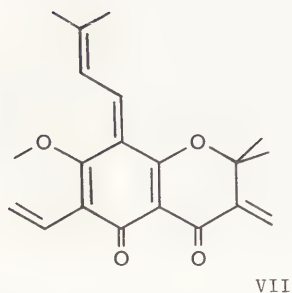
Spraying with 5% aqueous ferric chloride gave, as expected, blackish spots for all phenolic compounds tested, with no reaction for any non-phenolic compound tested. This may be especially useful in investigating the presence of gamboge in varnishes, since varnish resins do not usually contain phenols. Many other yellow natural products that might be competitors in the paintings and prints field, however, are also phenols, which limits the capabilities of this method. It may have some value as a confirmatory test, nevertheless.

b. Antimony Trichloride

A recommended spray reagent for resins (15) is a saturated solution of antimony(III) chloride in chloroform, following by heating the plate at 100° C. The gamboge spots noted in Table 1 were unaffected by this treatment, but heavy applications did produce two spots, leading the gambogic acid and fluorescent (after this treatment) in long-wave UV; these were probably too weak to be useful diagnostically. The natural varnish resins noted above gave characteristically fluorescent spots, many of which were not found by the quenching effect under short-wave UV. It is notable that the ferric chloride reaction still works for gamboge after antimony trichloride treatment, so that in appropriate circumstances, both could be used in succession.

c. N-Bromoacetamide (NBA)

This is an allylic brominating agent, and the rationale behind its use was the hope that the allylic carbon atom marked 'a' in the structure (I - VI) for gambogic acid and its congeners could be brominated, when a subsequent dehydrobromination would yield a cross-conjugated semiquinonoid system (VII) possibly having a characteristic color or fluorescence. In fact, when a developed gamboge plate was sprayed with 2% NBA in glacial acetic acid, then heated at 100° C for 10 minutes, the spots reacting positively to ferric chloride displayed a white fluorescence in long-wave ultraviolet radiation. The plate as a whole developed a rather weak greenish-yellow fluorescence. The yellow color of the gamboge spots (where the application was heavy enough for them to be visible) became less intense after NBA treatment but was otherwise unchanged.



VII

The importance of this reaction may lie partly in its relative sensitivity (see below) and partly in affording a plate reaction that may help in distinguishing gamboge constituents from other, and perhaps unexpected, compounds. In particular, it appears useful when faced with the possible presence of flavonoids, a group of yellow plant products several of which are known as dyestuffs. The flavonoids that we have been able to check have become more deeply colored after spraying with NBA (in the case of quercetin turning quite black), and under long-wave UV examination usually quench the greenish-yellow fluorescence of the plate. At the time of writing, this spray method had been developed only recently, and we still await further experience with it.

2. Sensitivity

In order to compare the sensitivity of different methods, solutions of gamboge of 1%, 0.1% and 0.01% were made up in methylene chloride (in which the gum component is, of course, insoluble). Measured volumes of these solutions were spotted on to the plates, to give gamboge applications ranging from 100 µg (10 µl of 1% solution) down to 0.1 µg (1 µl of 0.01% solution). These masses are purely nominal, being based on the total masses of gamboge originally weighed out to make up the solutions, and would therefore be overestimates of the masses of yellow resinous material present.

Two plate sizes were used in sensitivity measurements: 20×20 cm plates, on which the solvent front took about 2 hours to migrate approximately 150 mm, and 10×5 cm plates, on which the solvent front took 15-20 minutes to migrate approximately 75 mm. As expected, the latter, on which the spots have much less time for random diffusion or "spreading", showed measurably better sensitivity. The nominal masses of gamboge applied were 100, 30, 10, 3, 1, 0.3 and 0.1 µg. Sensitivities were compared by observing the lightest application at which the main spot was detectable (Table 2).



TABLE 2

Smallest nominal mass ( $\mu\text{g}$ ) for which main gamboge spot was just detectable

	<u>20×20 cm plate</u>	<u>5×10 cm plate</u>
Visual inspection	Usually 10	3
Short-wave UV*	1	0.3
Aqueous $\text{FeCl}_3$	3 (marginal)	1
N-Bromoacetamide	1	0.1 (marginal)

\*On fluorescent plates

It is seen, that as far as sensitivity is concerned, the NBA spray method is comparable to, and perhaps slightly better than, quenching of the plate fluorescence under short-wave UV. It is also possible to check plates in both of these ways. Ferric chloride spraying was, perhaps surprisingly, not as good. The shorter plates afforded a definite sensitivity increase over the larger.

In an attempt to relate the sensitivity question more directly to the problem of sampling a painting, a gamboge suspension was painted on to a ground of precipitated chalk bound with gelatin to give a yellow color of Munsell hue 3.7Y, chroma 10.0 and value 8.6 (measured with a Minolta Chromameter CR100 using D-65 illuminant). Samples were taken by using a sharpened piece of stainless steel hypodermic tubing to punch out discs of 0.5 mm diameter, which were extracted with dichloromethane or ethanol and the extracts spotted on to silica gel plates as before. The results are presented in Table 3, the two smallest samples were obtained by extracting one removed disc with a measured 10  $\mu\text{l}$  of ethanol, and spotting 6  $\mu\text{l}$  and 2  $\mu\text{l}$  of the extract respectively.

TABLE 3

Number of spots visible on 5×10 cm silica gel plate

No. of discs extracted	Area ( $\text{mm}^2$ )	No. of spots visible	
		Short-wave UV	NBA spray
4	0.79	4	-
2	0.39	3	-
1	0.20	2-3	2
1×0.6	0.12	1	2
1×0.2	0.04	1	1

These results can give at best only an approximate indication of the sampling requirement from a real painting. They suggest that this is not likely to be impossibly large, but does appear larger than is usual for inorganic pigments. From visual inspection, a circle of diameter 0.5 mm is about an order of magnitude greater than the area we have usually disturbed for inorganic samplings for identification.

#### Results from Paintings

A total of nine samples taken from eight Japanese paintings of the ukiyo-e school were extracted into dichloromethane and investigated by TLC on 5×10 cm plates under the conditions given above. These results therefore complement those published by FitzHugh for this collection of ukiyo-e paintings (3). All plates were checked under short-wave UV and by the N-bromoacetamide spray method. Those paintings affording samples that gave at least one spot corresponding to a gamboge standard are listed in Table 4.

TABLE 4

Freer ukiyo-e paintings showing gamboge by TLC method

<u>Accession No.</u>	<u>Description</u>	<u>Notes</u>
98.420	Utagawa Kuniyuki, hg, 19th c.	Over shell white
03.208	Unknown artist, sc, 17th c.	Over shell white
05.234	Hiroshige II, hg, 19th c.	-
57.2	Shunman, hg, late 18th-early 19th c.	Mixture with indigo

(sc = folding screen, hg = hanging scroll)

The remaining five samples (from four paintings) failed to yield definite evidence for gamboge; hence either this pigment was not present, or the sample contained insufficient for it to be detected. This last statement may define the principal weakness of TLC as used in this context for this purpose: a negative result may not always imply that gamboge was not used on the area of the painting sampled.

### Conclusion

Any investigator must be alive to the possibility of being deceived by an unexpected compound that happens to mimic the one being sought in the context of the methods being used. Nevertheless, our experience so far suggests that, provided sufficient sample is available, gamboge can be reliably distinguished by TLC from most other organic yellows that are at all likely to be present. A cautious approach in this regard is necessary when investigating painting materials from relatively early times where existing writings may be based more on supposition than on hard evidence.

The main difficulty with the TLC approach may lie more in the realm of sensitivity. It appears that the smallest detectable gamboge samples (using the techniques described above) require heavier sampling than we have usually been accustomed to do for the identification of inorganic pigments. Nevertheless, samples needed are not impossibly large, and we intend to pursue this as routine laboratory technique, at least for the more favorable cases. It seems clear, however, that the identification of organic colorants on East Asian paintings is likely to need other methods in addition.

Our investigations of gamboge in the context of varnish resins (as noted previously, gamboge is known to have been used as a varnish colorant) suggest that TLC also should be a practical method for detecting its presence here, but this lies outside our main concern at the Freer Gallery of Art, and we have not pursued the question in more detail.

### Acknowledgements

Mary W. Ballard of the Conservation Analytical Laboratory, Smithsonian Institution, performed color meter readings on a gamboge paint-out. Dr. I. O. Sutherland (then of the Department of Chemistry, Sheffield University, England) kindly supplied a sample of the pyridine complex of gambogic acid (see reference 19).

### References

1. Yamasaki, K., Emoto, Y., 'Pigments used in Japanese painting from the protohistoric period through the 19th century,' Ars Orientalis, 1979, vol. 11, 1-14.
2. Winter, J., 'Pigments in China - a preliminary bibliography of identifications,' ICOM Committee for Conservation Report 84/19/11-12, Copenhagen 1984.
3. FitzHugh, E.W., 'A pigment census of Japanese ukiyo-e paintings in the Freer Gallery of Art,' Ars Orientalis, 1979, vol. 11, 27-38.
4. Akiyama, T., 'X-ray experiments on the "Illustrated Ingakyō sutra," the scroll painting "Murasaki Shikibu nikki" and the "Resurrection of Buddha,"' Bijutsu Kenkyū, 1953, No. 168, 131-138.
5. Oguchi, H., Hayashi, I., 'On the coloring materials and painting techniques of artifacts unearthed from the tomb of the T'ang dynasty at Turfan,' Bulletin of the Department of Fine Arts, Tokyo University of the Arts, 1981, vol. 16, 1-40.
6. Hsü Wei-yeh, Chou Kuo-hsia, Li Yün-ho, 'X-ray analyses of the organic Tun-huang pigments,' Tun-huang Studies, 1st Issue, Dec., 1983, pp. 187-197 (published by Kan-su People's Publishing Co., Lan-chou, China).
7. Taguchi, E., Taguchi, M., 'Spectrophotometric identification of color materials, especially of organic pigments and combined mixed colors - with reference to the pigments used in the scroll "Genji monogatari 54-jo emaki" of Edo period,' Kobunkazai no Kagaku, 1977, Nos. 20-21, 18-37.
8. Asahina Yasuhiko, Shōsōin Yakubutsu (The Shōsōin Medicinals) Osaka 1955; see p. 493 for English summary.
9. Akiyama, T., 'The construction and colour of the "Moon Disk" inscribed with two Dharani of Amitabha in the Hōdō, Byōdō-in monastery,' Bijutsu Kenkyū, 1955, No. 182, 51-68.



10. Waley, A., A Catalogue of Paintings recovered from Tun-huang by Sir Aurel Stein . . ., London, 1931; see Introduction - Pigments, pp. xlvii-xlviii.
11. Akiyama, T., 'The use of violet color in Japanese painting of the 8th through the 12th century,' Bijutsu Kenkyū, 1962 No. 220, 1-22; idem., Secular Painting in early Medieval Japan, Tokyo 1964, chapter 4, for summary in French see p. XVIII.
12. Winter, J., 'Gold in Japanese paintings: a case history involving the kirikane technique,' in P. A. England, L. van Zelst (eds.), Application of Science in Examination of Works of Art, Proceedings of the Seminar September 7-9, 1983, Boston 1985, 46-54.
13. Feller, R. L., Curran, M., Bailie, C., 'Identification of traditional organic colorants employed in Japanese prints and determination of their rates of fading,' in R. S. Keyes, Japanese Woodblock Prints: a Catalogue of the Mary A. Ainsworth Collection, Oberlin, Ohio, 1984, 253-266.
14. E.g., J. H. Hofenk-de Graaff, W. G. Th. Roelofs, 'Preliminary report on the identification of yellow dyestuffs in ancient textiles with thin-layer chromatography,' ICOM Committee for Conservation, Report 69/17, Amsterdam 1969.
15. E.g., Stahl, E., Jork, H., 'Terpene derivatives, essential oils, balsams and resins,' in E. Stahl (ed.), Thin-layer Chromatography, A Laboratory Handbook, 2nd edn., Springer-Verlag, 1969, pp. 201-258.
16. R. D. Harley, Artists' Pigments c. 1600-1835, a Study in English Documentary Sources, 2nd Edition, Butterworths 1982, 104-107.
17. E.g., W. T. Brannt, Varnishes, Lacquers, Printing Inks and Sealing Waxes . . ., Philadelphia, 1893.
18. R. J. Gettens, G. L. Stout, Painting Materials: A Short Encyclopaedia, Van Nostrand 1942, reprinted by Dover, New York, 1966, p. 119.
19. Ollis, W. D., Ramsay, M. V. J., Sutherland, I. O., Mongolsuk, S., 'The constitution of gambogic acid,' Tetrahedron, 1965, vol. 21, 1453-1470, and references cited therein.
20. Venkataraman, K., 'Pigments of Garcinia species,' Proceedings of the Indian National Sciences Academy, Part A, 1973. vol. 39, 365-381.





## SUMMARY

This paper summarizes recent research on the technique of Early Netherlandish canvas painting. It shows that such works are usually thinly painted with oil colors on finely woven, tightly sized linen, but the sample of ninety-five paintings show a variety of techniques. Some canvases were framed; others were not. Some canvases were coarse and loosely woven; others were painted in oil colors. A new finding is that as early as 1434, canvases were painted with oils in the Netherlands. Documents reveal another interesting feature: canvases are sometimes painted while they were wet.

## THE TECHNIQUE OF EARLY NETHERLANDISH CANVAS PAINTING: AN OVERVIEW

Diane Wolfthal  
Department of Art History and Archaeology  
826 Schermerhorn  
Columbia University  
New York, N.Y. 10027, U.S.A.

This paper will examine a long neglected subject: the technique of Early Netherlandish canvas paintings.(1) Only ninety-five such canvases painted between 1400 and 1530 survive, although originally such paintings were quite popular.

Early Netherlandish canvases must generally have been woven from flax, since Flanders was the center of the European linen trade and linen was plentiful there.(2) Contemporary documents at times specify toile or lynwaed as paint supports.(3) Early Netherlandish canvases usually are of plain weave, but a Lot and His Daughters in Siena, attributed to Jan de Cock, shows a twill weave. Thread counts per centimeter range from a low of 13 to a high of 40, but generally fall between 18 and 20. Early Netherlandish canvases show no standard size. Several of the larger canvases show seams, a practice mentioned by Cennini.(4)

In 1458, a court ruling proclaimed that the cloth painters of Bruges "shall be permitted to work on all kinds of cloth of old linen, two ells or less in length, provided that the pieces have no holes or patches."(5) This suggests that painters may have used substandard canvas, that was not only old, but also patched.

Canvases must have been stretched to facilitate painting. Art treatises mention three methods: nailing the linen to a frame, lacing it, and laying it out on the floor over woolen cloths.(6) No Early Netherlandish stretchers survive.

Art treatises also indicate that canvases were sized and the court ruling mentioned above confirms this.(7) It specifies the use of glue size and advises that "no more (canvas) shall be glued (lymene) than (painters) can really complete at one time."(8) In four canvases, sizing was detected.(9)

Canvas must have been sized. One contemporary treatise, that of Le Begue, reveals that artists were well aware of the flexibility and absorbency of linen and knew that sizing would inhibit these qualities.(10) Sizing was generally applied very thinly, and was probably of the same substance as the paint film, which was therefore indistinguishable from it.

The methods described by Cennini and Le Begue all characterize the binding methods as water soluble, rather than oil. Cennini specifies egg tempera. Le Begue recommends glue, egg, or gum. Several other manuscripts also specify water soluble paints for canvases.(11)

Inventories at times specify the medium of canvas paintings. There can be no doubt of the meaning of "een cleet water varwe" or paintings "fait sans huelle et sur toile" or "a colla."(12)

Most fifteenth century Netherlandish canvases have a powdery, mat, thin appearance, consistent with glue tempera, as opposed to the glowing, translucent appearance of oil. Indeed paint samples from six works have been analyzed. These samples proved to contain a tempera binding medium.(13)

One unexpected finding is that oil colors were at times applied to linen. Documents reveal that flags were sometimes painted in oils, but, more importantly, a painting proper, a Crucifixion with four figures, now lost, was executed in 1434 at Ghent with oil colors. This date, 1434, is somewhat earlier than the one recently proposed for the earliest use in the Netherlands of oil painting on canvas.(14)

Further evidence of the early use of oil on canvas is found in the legal decision of 1463 involving the panel painters and cloth painters of Bruges. The court ruled that "painters on cloth shall not be permitted to work on cloths with any oil colors."(15) The implication is that painters wanted to do so, or were already doing so.

David's Deposition in New York may well be the earliest surviving Early Netherlandish canvas painted with oils. Suhr argued convincingly that the present canvas is original: "The paint follows exactly the variations of the weave in the canvas."(16) Furthermore, the presence of a black painted border and of a seam eighteen inches from the bottom, as well as a series of horizontal cracks at the center right edge, presumably caused when the painting was creased while rolled, confirms the originality of the canvas. The paint has never been tested to

determine its binding medium, but its appearance shows many characteristics of oil. Colors are not mat and powdery, but shiny and glowing. Thick ridges of individual brushstrokes are clearly visible. Eight other canvases may also have been painted in oil, but the preferred medium was doubtless tempera.

Following the research of Johnson, Packard and Kuhn, we must caution that even in Netherlandish canvases painted largely in tempera, there may be small areas or glazes of oil.(17)

Canvas painters seem to favor pigments that look best when mixed with tempera. Azurite, for example, which looks dark and muddy in oil, but sparkling in tempera, was detected in five out of six canvases tested. Azurite was singled out in Bruges legal decisions as a pigment that may be applied to linen.(18) Chalk, which is "useless" as a tone if mixed with oil, was detected in two canvases.(19)

A few canvases are painted in a thick, opaque fashion. In several cases, flesh tones are very thin, almost transparent, while the rest is thicker.

Generally, however, canvases were painted very thinly. Le Begue emphasizes that if his instructions are followed, the completed work will be thin and lacking in body.(20) Early Netherlandish canvases are usually so thin that the texture of the canvas is visible through the sizing and paint film. Some canvases, when held up to the light, become transparent. A thin canvas, with paint absorbed into its fabric, is more supple, and for this reason will be less likely to flake off.

One little known practice that emerges from documents is that canvases could be painted while wet. Cennini notes with pleasure that canvases, like fresco, remains moist during painting. The Bruges legal decision of 1458 requires that canvases "shall be ...worked while wet in the threads."(21)

Many canvases have painted borders, usually solid black or brown, but occasionally more ornate. Generally, when borders are lacking, the painting has been cut down. Certainly flags, banners, funerary palls, and tapestry substitutes painted on canvas were not framed. Cennini mentions that canvases were at times rolled or folded and some canvases show creases from folding.(22) Borders may have had an aesthetic appeal. Black, for example, deepens and enriches other colors.

Other canvases were certainly framed, as documents show.(23) At least one Early Netherlandish canvas may still be in its original frame.(24) Other canvases were early on attached to a board. Existing examples survive and documents also mention this practice.(25)

Certainly there was variety in technique. Some canvases were coarse or loosely woven, some painted in oil; some were framed, others not. The typical canvas, however, was thinly painted with glue colors on finely woven, lightly sized linen.

Compared to panel, canvas was easier and faster to paint. Rather than simply sewing pieces of cloth together to form a large support, painters had to glue planks of wood together. For canvas, painters applied only a thin layer of sizing; for panels they first used a thick, whitish ground composed of a layer of chalk and animal glue, and then applied a second layer impregnated with drying oil. Further speeding up the process, canvas could be painted while wet. Finally, the paint applied to canvas was often extremely thin, hardly covering the linen at times, whereas that applied to panel was built up slowly layer upon layer. Sometimes the paint itself was applied more rapidly on canvas than on panel.

Light in weight, canvases served as flags, banners and stage decorations. Flexible, they served as funeral palls. More durable than paper, they functioned as maps. Easily rolled and folded, they were ideal for export. Most importantly, since they could be painted rapidly and easily, they functioned as inexpensive substitutes for panels and tapestries.(26)

Leaving aside Bouts' canvases, whose original arrangement is problematic, the earliest Netherlandish altarpiece painted entirely on canvas is Blondeel's Sts. Cosmas and Damian, dated 1523, today in the Church of St. Jacques in Bruges. Contemporary documents record no altarpieces painted entirely on canvas, only two sets of canvas wings.(27) Thin, flimsy, fragile, and inexpensive, canvases were generally not deemed worthy of an altarpiece. The technique of Early Netherlandish canvases is intimately linked to their function.

Time has had an especially disastrous effect on Early Netherlandish canvases. For this reason, it is very difficult to determine their original appearance. Originally colors were brighter than they are now. Canvases that are well preserved, or whose edges have been protected for years by frames, show fresh, sparkling bright colors. We must remember this when we look at the dulled, water-stained, ragged remains.



## NOTES

1. This subject will be dealt with in my forthcoming publication The Beginnings of Netherlandish Canvas Painting: 1400-1530 (Cambridge University Press, to be published) and "The Technique of Early Netherlandish Canvases," Le Dessin sous-jacent dans la peinture. Colloque VI (to be published). See also my article, "Early Netherlandish Canvases: Documentary Evidence," Annales d'Histoire de l'Art et d'Archéologie, Brussels, 8 (1986): pp. 19-41.
2. A. J. Warden, The Linen Trade (London, 1864) pp. 290, 319, 344.
3. W. Soil, Les Tapisseries de Tournai (Tournai/Lille, 1892) pp. 352-353, 371-372; A. de La Grange, Etudes sur l'art à Tournai et sur les anciens artistes de cette ville (Tournai, 1887/88) pp. 131, 144, 146, 263; C. Dehaisnes, Documents et extraits concernant l'histoire de l'art dans la Flandre, l'Artois et le Hainault avant le XVe siècle (Lille, 1886) I, p. 550; A van Werveke, "Een werk van de Gentsche schilders Agnes vanden Bossche," Bulletin der Maatschappij van Geschied en Oudenheidkunde te Gent, 16 (1908): p. 223. For other examples, see note 1.
4. C. Cennini, Il Libro dell'Arte, ed. by D. V. Thompson, Jr. (New Haven, 1932) vol. I, pp. 98-99, II, pp. 103-104.
5. Wolfthal, "Early Netherlandish Canvases: Documentary Evidence," pp. 21, 34-35.
6. Ibid., p. 29.
7. Ibid., p. 30.
8. Ibid.
9. Bouts Entombment in London, his Resurrection in Pasadena, Lucas van Leyden's Moses in Boston and Christ and Two Pilgrims in Brussels.
10. M. P. Merrifield, Original Treatises on the Arts of Painting (New York, 1967) vol. I, pp. 258-267.
11. Wolfthal, "Early Netherlandish Canvases: Documentary Evidence," pp. 30-31.
12. Ibid., p. 31 n. 55.
13. Bouts, Entombment, London; Hugo van der Goes, Passion Madonna, Nuremberg; Hugo van der Goes, Madonna and Child, Kassel; Netherlandish, Madonna and Child, Boston; Netherlandish, Crucifixion and Christ and Two Pilgrims, Brussels.
14. Wolfthal, "Early Netherlandish Canvases: Documentary Evidence," pp. 30-31.
15. Ibid.
16. Unpublished technical report, Frick Collection, New York.
17. M. Johnson and E. Packard, "Methods Used for the Identification of Binding Media in Italian Paintings of the Fifteenth and Sixteenth Centuries," Studies in Conservation, 41, 1971, pp. 145, 158; M. Kuhn, "Farbmaterial und technischer Aufbau der Gemälde von Niklaus Manuel," Maltechnik (July 1977) pp. 155-171.
18. Wolfthal, "Early Netherlandish Canvases: Documentary Evidence," pp. 31-32.
19. Bomford et. al., "The Techniques of Dieric Bouts: Two Paintings Contrasted," London. National Gallery. Technical Bulletin (in press) pp. 39-57.
20. Wolfthal, "Early Netherlandish Canvases: Documentary Evidence," p. 31.
21. Ibid., p. 30.
22. Ibid., p. 32.
23. Ibid., pp. 32-33.
24. Netherlandish, Madonna and Child, Volterra, Pinacoteca.
25. M. Schayes, "Extrait des comptes et inventaire de la maison de Corneille Haveloes," Compte rendu des séances de la Commission royale d'histoire ou Recueil de ses Bulletins (1838): pp. 158-166.

26. For its lower price see, among others, H. Loriguet, "Les Tentures de haute-lisse possédées par l'abbaye de Saint-Vaast," Revue de Pas de Calais, Arras (1884): pp. 11-12; E. Muntz, Les Collections des Médicis (Paris/London, 1888) p. 58; E. K. Reznicek, "Eenkele Gegevens uit de vijftiende eeuw over de vlaamse schilderkunst in Florence," in Miscellanea Jozef Duverger (Ghent, 1968) I, p. 85; Schayes, "Extraits des comptes et inventaire," pp. 158-166.

27. M. de la Fons-Meliocq, "Eglise et bâtiments claustraux de l'abbaye de Saint-Bertin, aux XI<sup>e</sup>, X<sup>e</sup>, et XVI<sup>e</sup> siècles," Bulletin des comités historiques 2 (1850): p. 212; C. van Mander, Het Schilder-Boeck (Haarlem, 1604) fol. 236 (wings by Scorel).



# Working Group 2

Structural Restoration of Paintings  
on Canvas

Restauration structurale des peintures  
sur toile





## SUMMARY

A comparison has been made between two large and heavy contemporary oil paintings on canvas. The lined painting has no plane deformation while the unlined painting shows distinct signs of "sagging".

## TWO HEAVY CONTEMPORARY OIL PAINTINGS ON CANVAS: A COMPARISON BETWEEN LINED AND UNLINED

Marion Barclay  
Senior Conservator of Paintings  
Restoration and Conservation Laboratory  
National Gallery of Canada  
Ottawa, Ontario  
K1A 0M8 CANADA

## Introduction

At the International Symposium on the Conservation of Contemporary Art, held in Ottawa (Canada), July 1980, this author gave a paper on the initial research, describing in detail, the testing which had been carried out in developing a suitable structural treatment procedure for lining Milton Resnick's Saturn 1976 (2.5 X 3 m).<sup>1</sup> The following year this one-hundred-and-thirty-six (136) kilo oil painting on canvas was lined onto a rigid support. A brief description of the procedure used follows.

A fibreglass skinned aluminum honeycomb rigid panel was constructed in the Restoration and Conservation Laboratory (RCL) of the National Gallery of Canada (NGC). 2mm holes were drilled every 10 cm over the entire surface of the panel. An interleaf of polyester fabric (random weave) was adhered with Plextol B500.

Saturn 1976 was removed from its structurally inadequate stretcher and attached to a "dutch method strainer", which was in turn attached to a pulley system which had been installed in the ceiling of RCL. The painting was elevated in a horizontal orientation with a working surface the size of the painting below. Mylar was laid on top of the working surface with the rigid support on top of the mylar (raised 2 cm to allow easy withdrawal of the solvent vapour through the 2 mm holes in the rigid panel). Plextol B500 was then applied to the reverse side of the raised painting and then to the polyester interleaf (which had previously been adhered to the rigid support), and was left to dry for half an hour, allowing the water content to evaporate. The adhesive on the painting and the panel was reactivated using isopropanol; the painting was then lowered to the rigid support which was quickly sealed with double sided pressure sensitive tape attached to the perimeter mylar edges which were then extended up over the rigid panel onto the tacking margins to the edge of the face of the painting. Four vacuum hoses were connected into the sides of the mylar envelope, one at each corner of the painting. The hoses were hooked up to a large wet/dry shop vacuum for 24 hours to ensure contact and solvent removal between the painting and the panel support.

## Observation on Second, Unlined Treatment

The treatment on Saturn 1976 was so successful that the NGC was gifted in 1982 a larger second painting from the artist entitled That Elephant 1979 (3 X 4.8 m; 175 kilos). This painting came to the NGC rolled (as it had been for the previous three years) and has to this day, two vertical "flat" spots resulting from the pressure of lying in one orientation for the three years. That Elephant 1979 was unrolled, flattened, then stapled to a panel stretcher without the use of an adhesive.

The painting was exhibited and within a few weeks, it was apparent that the auxiliary panel was not supporting the painting effectively. That Elephant 1979 began to show an enlarging "beer-belly" in the center lower section of the painting, and draws were appearing in the upper left and right corners.

Due to the painting's "sagging" condition, a conservator-artist-curatorial consultation recommended an attachment of the painting to a panel support similar to that made for Saturn 1976. Due to time constraints, the panel support with fibreglass skins for That Elephant 1979 will be contracted out to a local conservator, but will have additional metal supports attached diagonally on the back as it has been noticed that Saturn 1976 tends to torque when being moved. The polyester fabric interleaf will be used as before but Plextol D360 will be utilized instead of Plextol B500 due to its superior adhesive and handling qualities. Although both Saturn 1976 and That Elephant 1979 have been painted quite recently, the traditional fabric support cannot support the weight of the oil paint.

## Notes

1. M.H. Barclay, "The Final Report on a Stabilizing Treatment for an Unusually Large and Heavy Contemporary Oil Painting on Canvas" (paper delivered at the 7th Triennial Meeting of the International Council of Museums Committee for Conservation, Copenhagen, September 10-14, 1984), p.84.2.3.

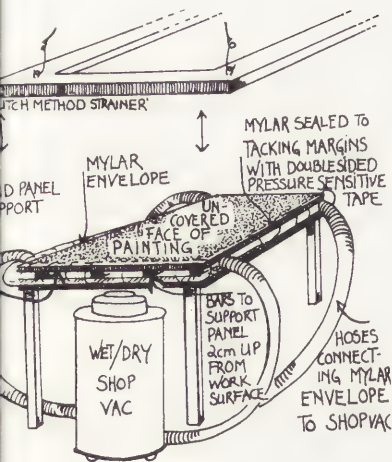


Diagram showing lining procedure.





## SUMMARY

Methods of structural conservation of canvas paintings are examined in the light of extensive stress measurements taken by the Berger-Russell Stress Tester for Stretched Canvas. The following samples were used: 1) Acrylic painting on sized linen fabric, especially prepared for this project in 1986. It was tested both before and after lining with BEVA 371, 2) Discarded passive oil-painting, signed and dated 1974, tested with and without the spring-loaded stretcher, 3) Discarded 17th century Spanish painting with old Italian pasta-lining. This sample underwent five different series of tests: a. with the glue-lining on, b. after removal of the glue-lining, c. supported by springs to simulate the self-adjusting, uniform-tension stretcher, d. its back coated with BEVA 371, and e. BEVA-lined. The different series of tests performed on the same sample represent various conservation treatments.

The tests produced widely divergent stress patterns in response to the various treatments and exposure to controlled environmental changes. Repeatedly the tests have shown a considerable reduction in stress fluctuations following lining and/or suspension from the self-adjusting, uniform-tension stretcher, as demonstrated by the computer graphs. These tests have shown that it is possible to measure directly the responses of canvas paintings to environmental changes. They also show that it is now possible to measure the reactions of canvas paintings to various conservation treatments. Some suggestions on how to utilize these tests in order to prevent or, at least, delay the decay of canvas paintings are offered.

## SOME CONSERVATION TREATMENTS IN THE LIGHT OF THE LATEST STRESS MEASUREMENTS (PRELIMINARY REPORT)

Gustav A. Berger  
Director of Research  
Art Conservation Research Foundation, Ltd.  
115 West 73rd Street  
New York, N.Y. 10023-2940, U.S.A.

William H. Russell  
Prof., Georgia Institute of Technology  
College of Architecture  
765 Yorkshire Road, N.E.  
Atlanta, Georgia 30306, U.S.A.

Introduction

The detection of frequent and sometimes violent stress changes in the surface of canvas paintings by the Berger-Russell Stress Tester for Stretched Canvas made it possible to analyze the behavior of canvas paintings in an entirely new way (1). Some of the forces which lead to the physical decay of paintings, and possibly all surfaces exposed to changing environmental conditions, can now be measured either directly or indirectly. A new tool has been developed to observe and compare the forces which act within the surfaces of all materials and particularly canvas paintings. This report is an attempt by the authors to interpret some of the findings collected since the beginning of this research project.

Stress measurements of stretched canvas samples representing paintings began six years ago. During this period thousands of tests have been performed, and an abundance of original data collected, some of which have already been published (1,2,3,4).

However, with the stress tester working twenty-four hours a day, producing ever more information, the authors face an overwhelming task: They have invented a 'barometer for paintings' but are painfully aware of the fact that 'weather-charts' which interpret the results may still be many years away.

The highly sensitive measurements of our stress tester show very clearly the reactions of paintings to treatments and to small changes in the environment. For this reason, we believe that they will be accepted and continued in the years to come. Because our interpretations are still mostly intuitive or based on incomplete evidence due to the novelty of this research, they will have to be further refined, while some might even be refuted. Therefore, this report will be confined to the most striking examples, where the readings of the stress tester confirm the experience of paintings' conservators.

The following conservation treatments have been selected for evaluation:

- I. Heat treatments
- II. Solvent and vapor treatments
- III. Support types:
  1. Lining, or Flexible Supports
  2. Solid Supports
  3. Uniform-Tension Stretcher

I. Heat Treatments

Treating paint and paintings with pressing irons, heated spatulas, hot-tables, and lately also hot-air blowers, are common practices in conservation. This research has shown that application of heat affects all the components of a painting (3).

Heat softens the painting and makes it pliable even if the humidity drops, as it must do in the case of hot-air treatments or in most operations on the vacuum hot-table, with heated spatulas, or irons (Figures 1a, 1b and 2a, 2b). In the presence of water or other solvents, the Tg\* of the materials is often reached or

---

\* At its glass transition temperature (Tg), which occurs at a fairly narrow temperature range, a polymer changes from an elastic and brittle solid into a malleable plastic material. The secondary crosslinks between the long polymer chains break under the increase of molecular movement caused by the elevated temperature. The material can then be deformed by a fraction of the force which would be needed at slightly lower temperatures (5).

exceeded (5,6). This means that their crosslinks are dissolved and their plastic reformation facilitated.

(Text continues following Explanations to the Figures on this page)

# REDUCTION OF TENSION WITH RISE IN TEMPERATURE

Fig.1a: Changes in Temp. & R.H.

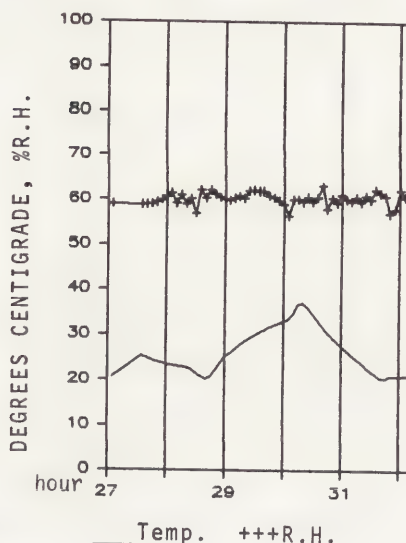
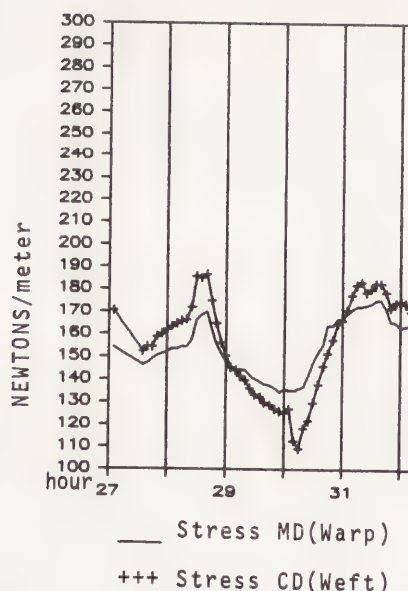


Fig.1b: Changes in Tension Due to Above Conditions



# REDUCTION OF TENSION WITH RISE IN TEMPERATURE

Fig.2a: Changes in Temp. & R.H.

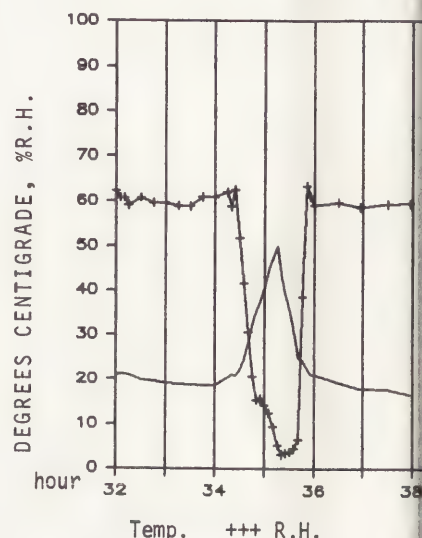
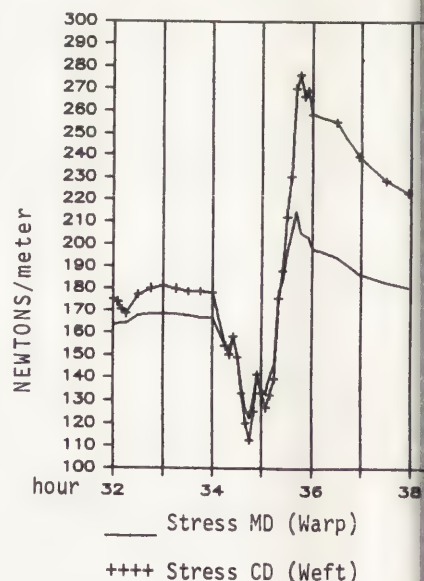


Fig.2b: Changes in Tension Due to Above Conditions



Figures 1a, 1b, 2a, and 2b show stress variations in response to changes in temperature and relative humidity. All refer to a segment of a particular test series, during the period beginning at the 27th hour of testing and ending at the 38th hour.

Prior to this test, the sample was conditioned at about 21°C and 60% R.H. At about 28.7 hours, the temperature was raised to about 40°C while the R.H. remained constant at 60% (the hours can be read along the bottom line of the graph).

Fig.1a (top, left), 28h-32h - The temperature is raised from 20°C to 37°C, while the R.H. is kept constant at 60%.

Fig.1b (bottom, left) - Changes in tension caused by the rise in temperature shown in Fig.1a. The tension drops from appr. 180 N/m to 110 N/m, but returns to the previous values after cooling.

Fig.2a (top, right) - The temperature is raised from 20°C to 50°C and the R.H. is lowered to 3% to simulate conditions on the vacuum hot-table.

Fig.2b (bottom, right) - The resulting changes in tension: the stress drops with the rise in temperature to 30°C and reaches the same level as before (115 N/m). However, thereafter, the stress begins to rise rapidly (almost doubles in the MD direction). Even when the sample returns to the previous R.H. of 60%, it takes many hours for the tension to drop to its original value (between 150-170 N/m).

Sample: 17th century Spanish Painting, Glue-Lined.

In other words, deformations such as kinks, blisters, and cupping can be straightened. The usual result of heat treatment is that the tension in the canvas is reduced as the paint-film swells in volume and thereafter becomes compressed in the lateral direction. This is shown in Figures 3, 4, and 5, where the shrinkage of the canvas had caused enormous blisters in the paint-film. Following treatment with heat and pressure, these blisters shrank to such an extent that the paint-film became shorter than the canvas, causing the laminate to bend upward upon cooling (Fig.4). Such shrinking of the laminate by heat treatment (also documented in Figures 9 and 13) is the main reason why conservators are able to eliminate kinks and bumps by ironing a deformed canvas. Were it not for the resulting shrinkage, even extreme pressure could not straighten a deformed painting without loss of paint. This is why it is impossible to eliminate similar deformations on painted metal plates, as any conservator who has tried to straighten and remove bulges on a deformed painting on metal can readily confirm. The cooling which follows exposure to elevated temperature (heat treatment) causes increased stress in the sample painting, as can be clearly



Explanations to Figures  
3, 4, and 5

Fig.3 - A 19th century Mexican oil-painting on a "shrinking" canvas, 20x36cm.

The shrinkage of the canvas has caused enormous blisters in the paint film, which could not follow the resulting compression, and became much larger than the supporting, shrunken, canvas. Please, note the blistering along the edge of the stretcher (discussed under II.2).



Fig.4 - Same painting as in Fig.3. "Stretching" of the canvas and heat treatments on the vacuum and suction tables made it possible to reattach the blistering paint. However, the paint-film has now been compressed, and become shorter than the canvas. Upon cooling, the canvas cups upward, giving the paint-layer a concave form.

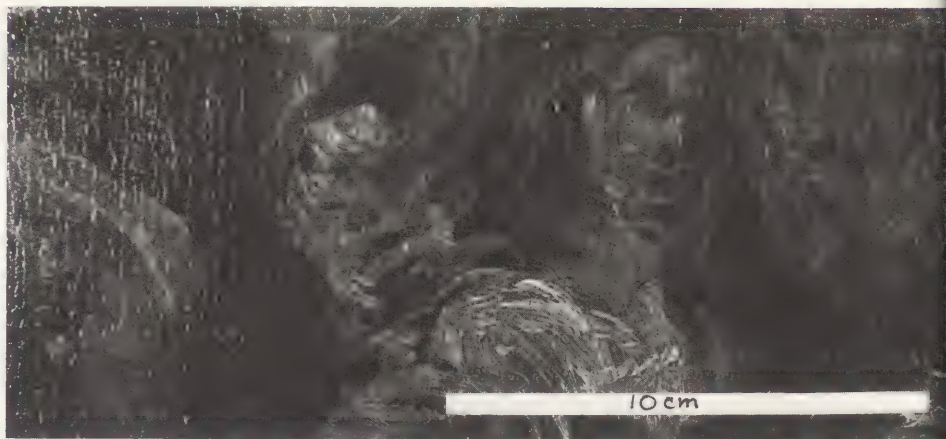


Fig.5 - Same painting as in Figures 3 and 4. Following lining, it shows that a paint-film can sustain and support enormous deformations during its life time and treatments.





**Fig.6 (Top, right)**  
Sample drawn from a 17th c. copy of "The Spinners", by Velasquez. It was used in the test series, a segment of which is shown in Figures 1, 2, and 9 through 13.



seen in Figures 2, 9, and 13. This increased stress attests to shrinkage of the sample following heat treatment. It shows an excellent corroboration between the findings of this research and the experience of practicing conservators. The sample shown in Figure 6 maintained the rise in tension from 140 N/m to 180 N/m for several weeks until the test was discontinued (shown on Fig.13).

Heat treatment is indeed a very effective tool against blisters because it shrinks the paint-layer which is softened and compressed in the process. However, heat treatment, actually repeats the circumstances leading to cupping which is caused by the shrinkage of the top layer of the paint. In order to remove cupping and to bend the paint-film back into position, compression of the bottom layer of the paint is required (Fig.4). Compression of the bottom layer can be achieved only if we succeed in swelling it in excess of the shortened outer skin which forms the top layer. Such selective swelling can be accomplished with the help of solvents, used in the form of "Vapor Treatments" (7).

## II. Solvent and Vapor Treatments.

### II.1 Treatment With Solvents.

In aged paintings, the top layer of the paint crosslinks more rapidly than the bottom layer because it is directly exposed to light and UV radiation. The bottom layer of the paint, being protected by the top layer, crosslinks less and, consequently, remains more susceptible to swelling by solvents. Therefore, solvents applied from beneath the paint layer swell the lower parts of the paint. This action alone would make the paint cup more, as can be demonstrated by applying "paint remover" to any aged paint (Fig.7). If the paint layer is held straight during solvent treatment - as it is on the vacuum hot-table - the swelled film will be compressed, and the cupping eliminated. However, treating paint and fabrics with solvents, particularly water, is not without hazards. This fact cannot be overemphasized, and has been repeatedly confirmed by our stress tests.

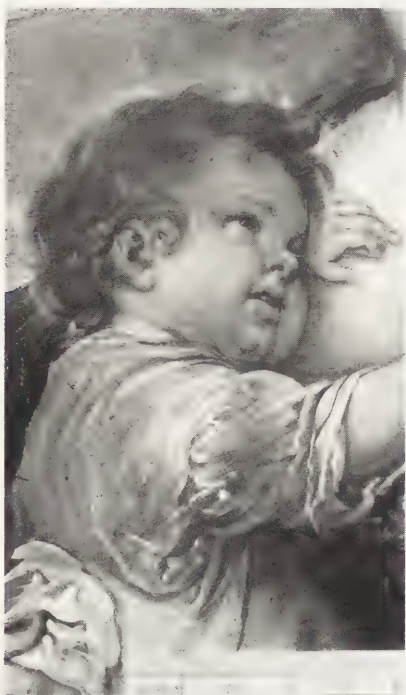
### II.2 The Effects of Humidity.

Most, if not all, natural fabrics shrink upon wetting. Cotton shrinks considerably, even at slight changes in R.H., linen and hemp shrink to a lesser degree, and burlap shrinks least of all. Of special interest to conservators is the considerable shrinkage displayed by all fabrics, except for burlap, when the R.H. rises above 80%, and the tremendous shrinkages which occur when the dew point is exceeded (1). In such cases, the shrinkage seems to exceed even that which takes place during outright wetting. If, under these circumstances, a fabric is restrained in its movement by a rigid stretcher, the tension can rise up to four times its normal value, and is usually the maximum tension a canvas can develop on its own. Such tension (stress) creates a force far greater than a canvas can sustain. As a result, the fabric is greatly over-stretched. Since it also becomes somewhat softer and often reaches its Tg (5), when the humidity rises, the fabric becomes plastically deformed (6). The canvas starts to 'creep', and increases in size (See also Fig.10, where such creep is actually documented by our tests).

A strong, prolonged contraction seems to be necessary to generate such a continuous and strong rise in tension, as is generated by rising humidity. The authors have measured the displacement necessary to generate a stress of this kind, and found that it is small indeed, especially in the cross-machine direction.



**Fig.7** - Paint-film expands when exposed to solvents (In this case - paint remover).



**Fig.8** - Detail of "Madonna and Child" by H. van Balen the Younger (1623-61), oil on copper, 35x25cm. Painting has neither significant cracks, nor disfiguring blisters.



In the 17th century Spanish painting, shown in Fig.6, a shrinkage of only 0.1% in the weft (CD) direction, raises the tension by more than 100 N/m (app. 10 Kg/m). This, in effect, doubles the tension a canvas of this type would normally sustain in its function as a support for painting.

However, at this tension the shrinkage must continue to increase if the stress is to remain the same, let alone rise, in order to make up for the losses in tension caused by the deformation (creep) of the canvas. If this increase in shrinkage stops, or is reversed, a rapid drop in tension takes place, and the canvas loses stiffness. It can no longer resist any stress put upon it by other parts of the laminate, particularly, the ones which are still shrinking under the influence of humidity. The rapid drop in tension following the cessation of exposure to high humidity is most pronounced in raw, unsized canvas or unlined paintings. It can be seen quite clearly in Fig.10 at the 63rd hour of this test. As a result of the rapid drop in tension, parts of the canvas are still shrinking while others have started to expand rapidly. The expanding parts no longer offer any resistance to the shrinkage of the canvas which contracts violently. The paint-film cannot follow this shrinkage; it lifts off in tent-like flakes and blisters, even if the painting is firmly held by a stretcher, or a supporting strainer (Fig.3). Thus, these tests have further confirmed the dangers of treating paintings with water-vapors or high humidity. Our investigations have shown that vapors are indeed powerful tools which enable conservators to correct severe defects in paintings, but great caution, experience, and further intensive study are required, before they can be generally recommended, or used with complete confidence.

### III. Support Types

One of the first questions which the previously described test results seem to raise is: Could weights, or springs, or even a rigid support prevent the dimensional changes of the canvas upon shrinking and the subsequent collapse of tension in the canvas? The answer seems to be positive. Various types of linings were examined: Italian pasta-linings, wax-linings, BEVA-linings, and finally canvases suspended from a simulated self-adjusting, uniform-tension stretcher. In each case of exposure to extreme conditions of either dryness or humidity, the reactions of the lined canvases were considerably reduced or, at least, delayed when compared with the test results on the same sample, before lining (See Table I and Fig.9-13).

The tests described in this report allow us to compare and evaluate different types of conservation treatments. To facilitate comparisons, only one sample, a typical Italian pasta-lining of a 17th century Spanish painting was used. The reactions of this sample to a predetermined set of environmental changes were measured and recorded. Then, the lining and glue were removed, and the new reactions of the altered sample were also measured and recorded. This permitted an evaluation of the effects of the glue-lining versus no lining. The following variations of treatment were measured:

- \* Pasta-lining (Fig.9),
- \* Pasta-lining removed (Fig.10),
- \* Spring-support in simulation of the self-adjusting stretcher (Fig.11),
- \* Reverse of the sample coated with BEVA (Fig.12),
- \* BEVA-lined (Fig.13).

To further facilitate comparison of the results, all the figures are presented in the same form and vertical scale. The top graph gives the changes in temperature and R.H. while the bottom graph shows the resulting changes in stress.

#### III.1 Lining or Flexible Supports

Lining often doubles, triples, and sometimes even more than triples the thickness of the laminate. This by itself slows down the reactions of the lined painting to changes in the environment, because of the time which elapses before such change can penetrate into the inner layers of the laminate (See Tables I and II, and Figures 9-13). In addition, the materials used as lining adhesives, especially wax and BEVA, act as moisture barriers, and protect the painting from the effects of humidity changes. This means that lining transforms the original canvas into a firmer support for the paint-film, similar to that of stone or metal plates.

#### III.2 Solid Supports

The unusually good state of preservation of paint-films on stone or metal plates provides proof that a firm support helps prevent their decay. Paintings supported by these materials have often remained in perfect condition for many centuries (Fig.8).

FIG.9 17th c. SPANISH PAINTING WITH OLD ITALIAN PASTA LINING

Changes in Temperature and R.H.

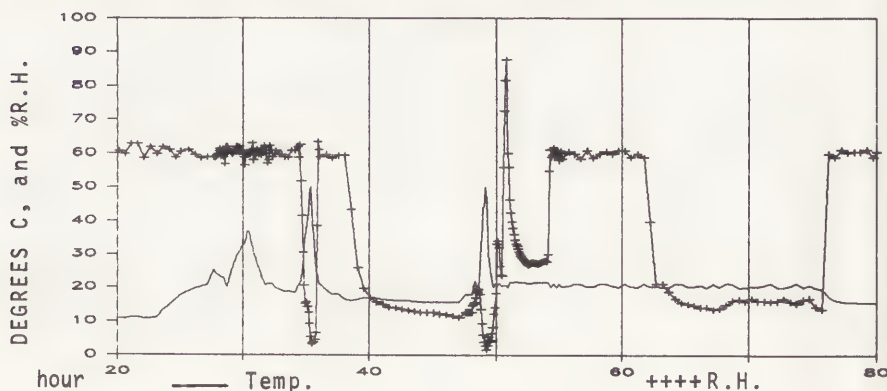


Fig.9 17th century Spanish painting, glue-lined (The first 27-38 hours of this test are shown in enlargement in Figures 1 and 2).

The stress variations are considerable. The fluctuations, however, are not as violent as in Fig.10, below, where the lining has been removed.

Please, note that in Fig.9 the largest rise in tension is at the high values of R.H.

Changes in Tension Caused by the Above Conditions

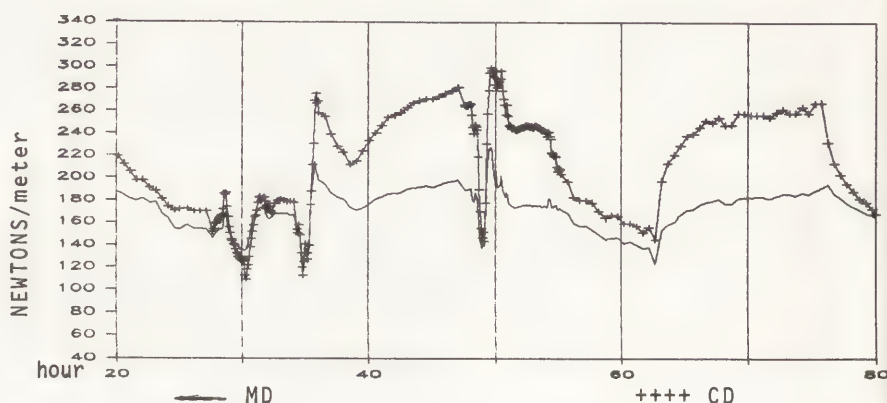
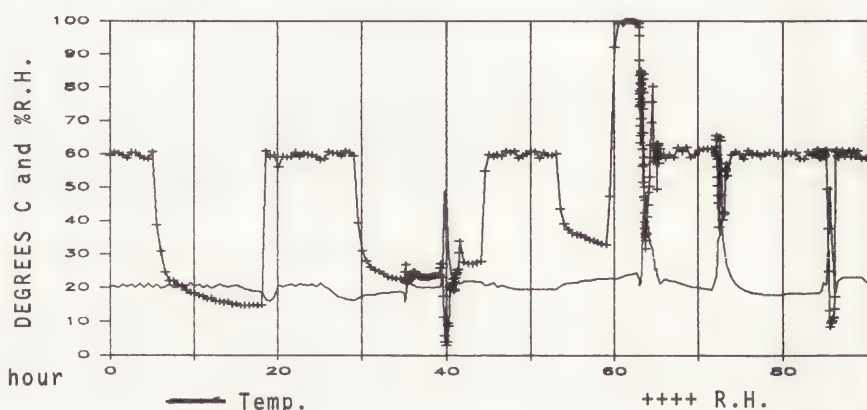


Fig.10 Same sample as in Fig.9, with the lining removed. A much higher and longer-lasting rise in R.H. at 60th h. fails to produce a comparable rise in stress. The canvas is already too weak to support this stress, and stays overstretched, with a resulting drop in tension. From the 65th h. on, the canvas fails to return to its previous values. This means that after one high humidity cycle the canvas has little tension left and, if it were a regular painting it would have to be "keyed out". It is noteworthy that in the unlined sample relatively small changes in temperature and R.H. can lead to disproportionately large changes in tension. This is especially evident at 35 h, where a small rise in temperature leads to a rather large stress change in CD.

FIG.10 SAME PAINTING WITH THE LINING REMOVED

Changes in Temperature and R.H.



Changes in Tension Caused by the Above Conditions

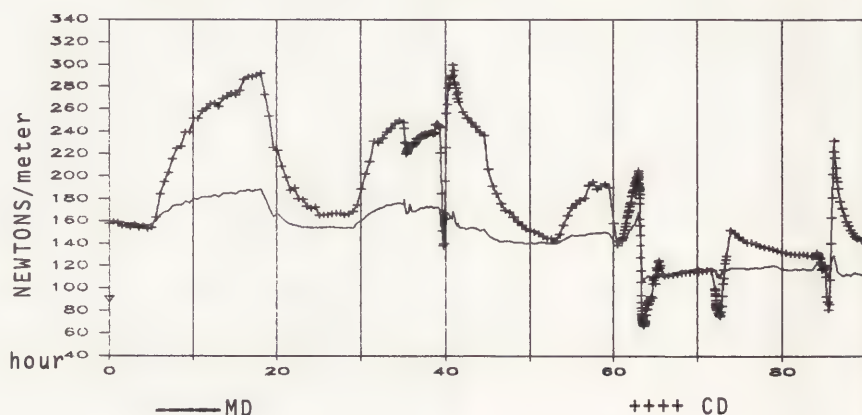




FIG.11 17th CENTURY SPANISH PAINTING SUPPORTED BY SPRINGS  
(Following removal of the glue-lining)

Changes in Temperature and R.H.

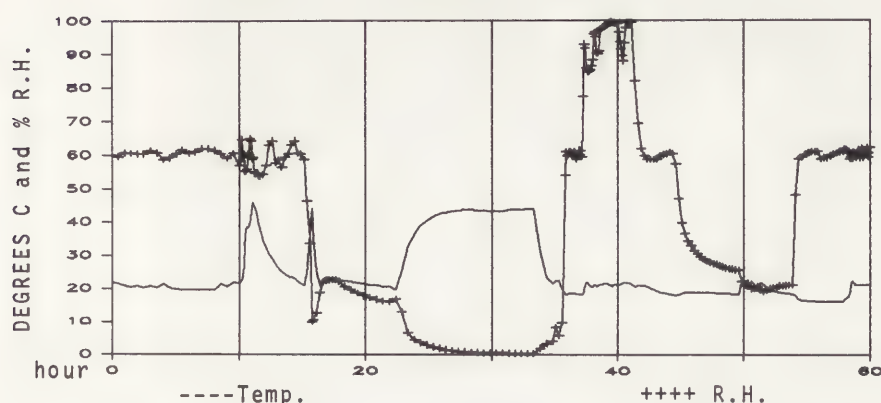


Fig.11 Same sample as in Fig.10, held by springs to simulate the uniform-tension stretcher. Although the sample is exposed to larger environmental fluctuations than before, the stress changes are almost completely absorbed by the springs. There is neither an increase nor a subsequent loss of tension, even after prolonged exposure to high humidity.

Changes in Tension Caused by the Above Conditions

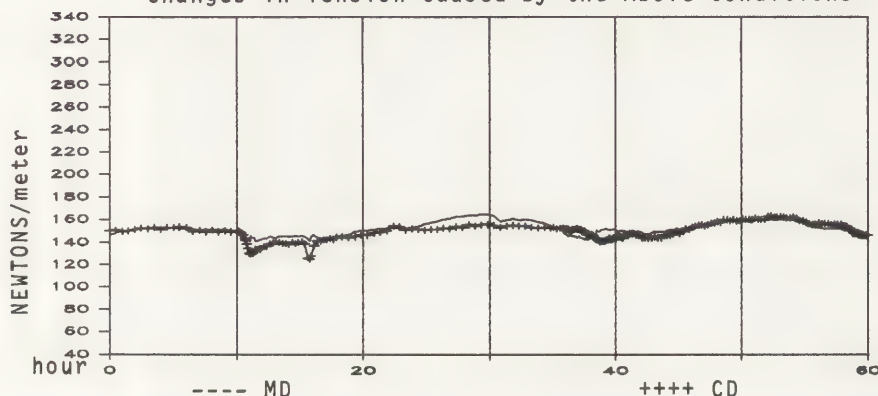
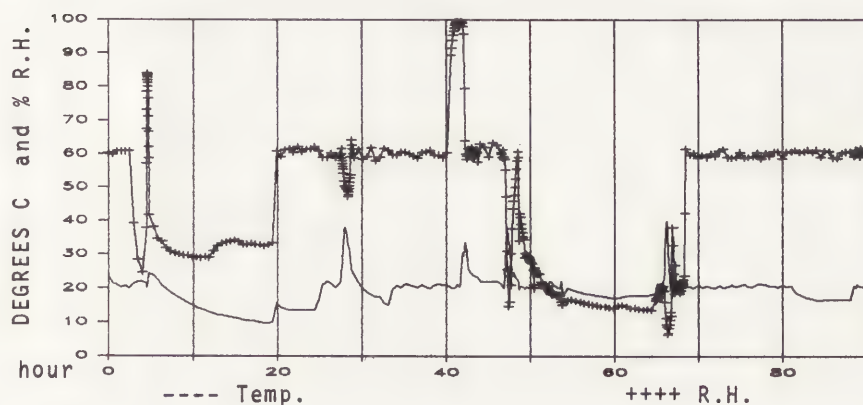


Fig.12 BEVA coating reduces the short-term effects of humidity changes, as shown by the gentler slopes compared to those of the unlined sample (Fig.10). (Wax coating would have a similar effect). Particularly striking is the reversal of the effect of high humidity at 40 h: The tension does not rise at all in response to a short rise in R.H. to 100%. However, because similar samples ruptured during long term exposure to high R.H., it was decided not to test this unlined sample too severely, except when supported by springs. In this sample, tension is lost after each cycle of changes (especially at high R.H.), and is much lower after only 80 h of testing than it was at the beginning of the test.

FIG.12 17 c. SPANISH PAINTING BACK COATED WITH BEVA 371

Changes in Temperature and R.H.



Changes in Tension Caused by the Above Conditions

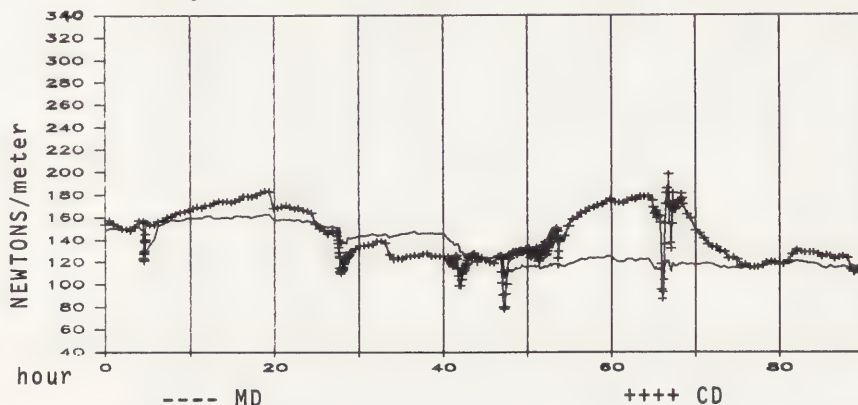
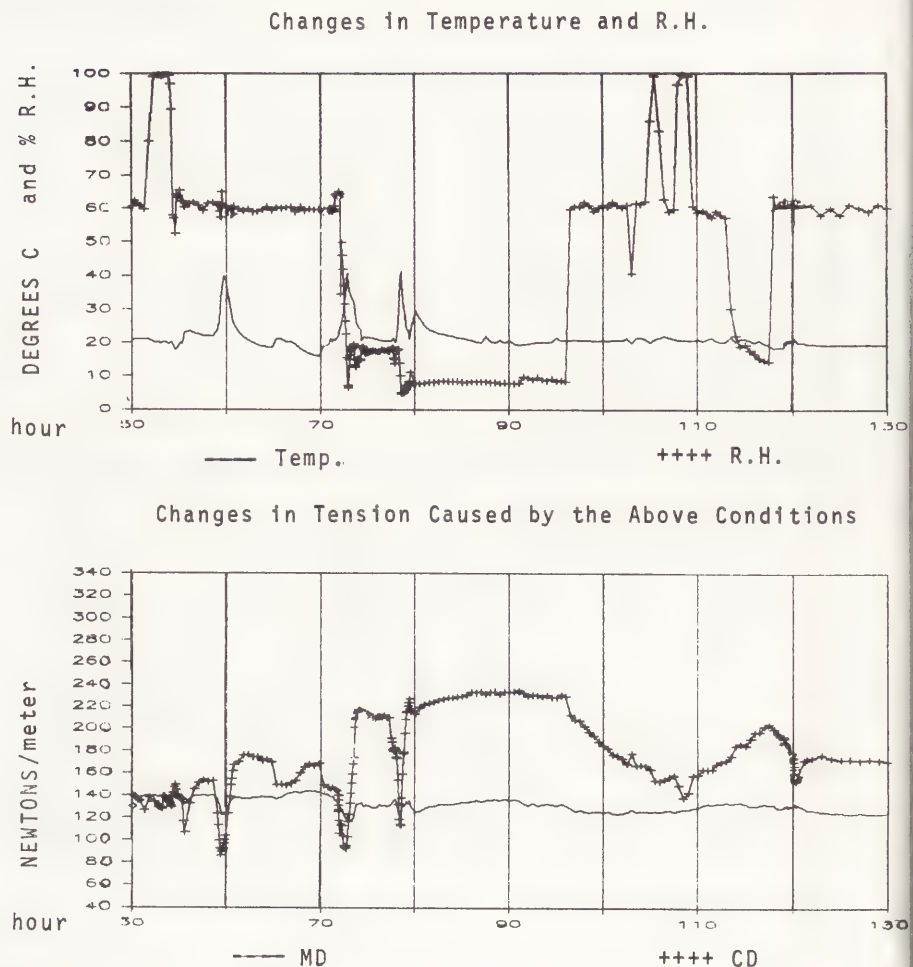


FIG. 13

17th CENTURY SPANISH PAINTING RELINED WITH BEVA 371

Fig. 13 Same sample as in Fig. 12, following relining with BEVA 371 on Polyester fabric and a Mylar (Melinex) interleaf. The stress fluctuations seem large. However, they should be divided by a factor of about 10, to account for the increased stiffness, imparted by the lining, which generates much larger forces than the soft fabric alone. In spite of this, the maximum difference between the highest and lowest stress is less than in both the glue-lined and the unlined samples. In addition, the stress changes are considerably delayed. The slope of the fluctuations is much more gradual, and small fluctuations, especially of humidity, cause hardly any stress changes. The reactions of the laminate to environmental changes have become more similar to the reactions of the paint than to those of the support to the same environmental changes. Of interest is also the observation that the stress is slightly raised after heat treatment. This effect lasts to the end of the test. For this reason, the laminate does not register any loss of tension after prolonged cycling, unlike the unlined sample.



Conservators treating canvas murals confirm their experience that the paint film is perfectly preserved as long as the canvas remains fully attached to the wall. The paint film usually cracks only in those places where the canvas has loosened from the wall.

### III. 3. Uniform-Tension Stretcher (8, 9)

An excellent example showing how the firmness of the support protects the life of the paint film, is a 17th century Spanish copy after Velasquez (Fig. 6). Our measurements show the vertical weft (CD) direction of the laminate to be about three times stiffer than the horizontal warp (MD) direction. Accordingly, the paint film cracked mainly vertically. This means that the greater flexibility of the warp direction of the canvas causes the paint film to break because it cannot restrain its movements. On the other hand, it is the uniform, continuous tension in the upper levels of panoramas which impedes the movements of the paint film and contributes to the survival of these paintings under the most adverse conditions. This seems to indicate that the life expectancy of a paint layer is much improved, if it is supported by a substrate which resists movement uniformly. Tables I and II and Figures 11, 12, and 13, show how lining and spring-loaded stretchers can reduce stress fluctuations in canvas paintings. The role of springs in the reduction of stress fluctuations is as striking as it is logical. The minute dimensional changes which cause dramatic stress fluctuations in canvas paintings confined by rigid stretchers can be readily absorbed by springs. Springs transform the canvas into a nearly inert substrate, on which environmental changes have little effect. Without necessitating costly air-conditioning, which often causes still more severe damage when it fails, it seems possible to prevent decay of paint films to a large extent by using the simple device of a spring-loaded stretcher. It is now possible to delay the decay of canvas paintings, and to protect them from unwanted and damaging interventions which become necessary once cracking, deformation and delamination set in.



TABLE I REDUCED STRESS VARIATIONS AFTER LINING AND USING SPRING SUPPORTS

(Typical stress for each pair of values in Newtons per meter)

Sample	Environmental Conditions	Temp. 21°C	R.H. 40%	Temp. 21°C	R.H. 60%	Temp. 21°C	R.H. 80%	Temp. 21°C	R.H. 99%	Temp. 35°C	R.H. 60%	Maximum Stress Variation*
	Acrylic	240 - 320		180 - 200		240 - 340		N.A.		150 - 160		190
a	Acrylic, Lined	170 - 180		145 - 160		120 - 140		120 - 140		80 - 100		100
	Oil-painting	160 - 180		140 - 150		300 - 320		320 - 340		135 - 145		205
a	Oil-painting, Spring-supported	219 - 220		195 - 205		189 - 191		178 - 182		178 - 182		42

Description of the samples:

- Acrylic painting on sized linen fabric, prepared for these tests, 1986,
- a - Sample #1, lined with Beva 371,
- Pastose oil painting, 1974,
- a - Sample #2, suspended from springs, to simulate the uniform-tension stretcher.
- Maximum Stress Variation - The difference between the highest and lowest values on the Table.

TABLE II NUMERICAL EVALUATION OF TEST RESULTS OF THE 17th CENTURY SPANISH PAINTING (Figures 9-13)

(Typical stress for each pair of values in Newtons per meter)

Sample	Environmental Conditions	Temp. 21°C	R.H. ca.15%	Temp. 21°C	R.H. 60%	Temp. 21°C	R.H. 80%	Temp. 21°C	R.H. 99%	Temp. 35°C	R.H. 60%	Maximum Stress Variation*
a	Pasta Lining (Fig.9)	240 - 311		160 - 180		280 - 305		N.A.**		100 - 109		201
b	Lining removed (Fig.10)	280 - 300		160 - 180		N.A.**		200 +		80		220
c	Unlined, Spring-Supported (Fig.11)	155 - 165		150		N.A.**		140 - 150		130		35
d	Unlined, Beva-Coated (Fig.12)	160 - 180		110 - 120		N.A.**		100		80		100
e	Beva - Lined (Fig.13)	200 - 220		160 - 180		140 - 160		140 - 160		80		140

Maximum Stress Variation - The difference between the highest and lowest values on the Table.

No values available.

Conclusions:

The findings of this research indicate:

- that creating inert supports, even for paintings which initially lack them, is now possible. By doing so, cracking, deformation and decay of the painting can be delayed;
- that it is possible to reduce tensions in paint films by appropriate conservation methods, of which heat and solvent treatments may be the most important.
- that it is possible to measure the efficacy of our conservation methods;
- that the described tests are a valuable tool in the analysis of the techniques and materials used in painting, and probably in materials, in general.

Conclusions (Continued):

In addition, we have already tantalizing views of other important findings, and a new understanding of the mechanism of decay in general, and of paintings in particular. The authors will report on those in the near future.

Acknowledgements:

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To all the other foundations, some of whom asked to remain anonymous, and to the other dedicated friends, too numerous to mention by name, gratitude is expressed.

## NOTES

1. G.A. Berger and W.H. Russell, "Investigations Into the Reaction of Plastic Materials to Environmental Changes. Part I: The Mechanics of Decay of Paint Films", Studies in Conservation 31, No.2 (1986), pp.49-64.
2. W.H. Russell and G.A. Berger, "The Behavior of Canvas As A Structural Support for Painting", in Science and Technology in the Service of Conservation (edited by N.S. Brommelle and Garry Thoms (1982), pp.139-145.
3. G.A. Berger and W.H. Russell, "The New Stress Tests on Canvas Paintings and Some of Their Implications on the Preservation of Paintings", (Paper delivered at the Seventh Triennial Meeting of the International Council of Museums Committee for Conservation, Copenhagen, September 11, 1984), pp.84.2.7 - 84.2.9.
4. R. Guilly, M. Sotton, and M. Chevalier, "Etude des proprietes de doublages experimentaux a la colle synthetique" (Paper delivered at the Sixth Triennial Meeting of the International Council of Museums Committee for Conservation, Ottawa, September 22, 1981), pp.31.5.1 - 31.5.13.
5. A.V. Tobolsky, "The Mechanical Properties of Polymers", Scientific American, September 1957, pp.121 - 134.
6. R.R. Bresee, "General Effects of Ageing on Textiles", Journal of the AIC, 25, No.1 (1986), pp. 39 - 48.
7. M.M. Watherston, "Treatment of Cupped and Cracked Paint Films Using Organic Solvents and Water", in Conservation and Restoration of Pictorial Art, (Brommelle and Smith, editors), Butterworth (1977), pp. 110 - 125.
8. G.A. Berger, "Winning Canvas Paintings' Battle of the Bulge... A Structural Alternative", Technology & Conservation, Spring 1983 issue (1983), pp.5-9.
9. G.A. Berger, "A Structural Solution for the Preservation of Canvas Paintings", Studies in Conservation, 29, No.3 (1984) pp.139-142.



## SUMMARY

For abrasive micro-friction methods for removal of glue and varnish, old retouching and fillings from painted surfaces can be useful and safe if the painting is physically suited to the treatment, and certain precautions are taken. Safe removal of surface accretions largely depends on the different degrees of brittleness of the layers. Hardened glue and varnish are usually more brittle than the original oil paint, but dangers can arise from internal weakness within the paint layers. The advantages of the method are evaluated and the conditions, which must be met, are listed.

REMOVAL OF VARNISH AND GLUE FROM PAINTED SURFACES  
USING MICRO-FRICTION

Pierre B. Boissonnas  
Westby Percival-Prescott  
Ateliers de Conservation  
Baschligplatz 1  
CH - 8032 Zürich / Switzerland

Introduction; Historical Background

The physical structure of a painting plays a decisive role in its appearance and artistic meaning. Actions such as cleaning, lining or the application of varnishes can alter the appearance of a painting significantly, particularly if it is a modern or contemporary work. Sadly few paintings continue to exist for long in their original state. After a few years the paint layers will have slightly changed their appearance, some become dull. The painting if not sufficiently protected, begins to look drab and the former colour values start to lose contrast. Deposits of dirt, grime, tobacco smoke or grease may still further diminish its original freshness. The time soon comes when a remedy is sought; usually a coat of varnish is applied bringing a further change to both the colour contrast, which is temporarily enhanced, and to the structure of the surface which is impaired. Reapplication of varnish brings further temporary improvement, but one application of varnish often leads to another and so gradually the painting becomes covered with layers of darkened coatings. Conservators then face the task of the removal of these unwanted layers without endangering the original painting.

If the work has been lined, traces of the lining paste or adhesives, consolidants and coatings, will also be present on the surface. The range of substances found on the surface of a painting of any age is very wide. It includes many types of oil, resin, glue, starch, gum, wax and grime. Some of these will have been acquired by chance; others applied as isolating coatings and by their combination produce a locking mechanism where the solubility of the individual components has been lessened or eliminated. For example, white of egg layers (glair) might have been applied below a layer of oil/resin varnish, (this was common practice in the eighteenth century) or a layer of glue size applied below a layer of mastic spirit varnish, (more usual in the nineteenth century). These are typical combinations. The twentieth century has added many more materials which in combination produce difficulties of solubility and reversibility.

Today a conservator is often faced with the problem of removing a formidable barrier of miscellaneous materials. Traditionally there are two ways of "cleaning" a painted surface. Mechanically (friction or even rubbing with fingers), or with solvents. The latter method is the most commonly used at the present time, but it is worth remembering the friction methods of varnish removal were widely used, and seriously advocated in the nineteenth century on the grounds of increased safety to the painting. Mastic varnish was commonly used at this time and could be pulverised from the paint surface by rubbing gently, leaving the painting completely unharmed. Those who have used this method will know the surprisingly good condition of the exposed paint.

In this paper we consider the possibilities of using similar methods of friction to remove many other types of brittle materials from the surface of paintings. For the past ten years we have examined this problem and have come to the conclusion that the principle of mechanical cleaning using micro-friction is a sound one and well suited to the removal of many brittle materials if the original layers of the painting have cohesion and elasticity. Fortunately the paint layers of many ancient and modern paintings have these characteristics and are quite suited to this method. In practice 20% of the paintings being treated are suited and many could not have been treated successfully in any other way. Naturally the means we use continue to be modified and adapted to suit the particular problem being posed by a painting. This will affect the choice of the air pencil and the size of the nozzle, the air pressure and the volume and type of abrasive powder. Air abrasive techniques have been used and refined over many years in the field of archaeological conservation, where they are regularly used to remove embrittled surface accretions and deposits from all types of artifacts, pigmented, corroded and otherwise.



A painting by Maurice Utrillo being cleaned using micro-friction. A fine jet of glass powder directed through an air pencil reduces the brittle and darkened layers of old varnish to an easily removable dust. The painting is being treated in a ventilated chamber with a plate glass window which can be swung open for access. Arm holes at the base of the chamber allow the operation to take place without the backward migration of the glass powder.

Detail of the painting by Utrillo showing the removal of the darkened varnish (left hand side). The exposed paint retains its delicate brush strokes and regains its original vitality.





### Photographic and Visual Examination

Photographic records should be made before and during treatment particularly of small areas where the paint is unusually thin or delicate. General views are always necessary, but lifesize details taken on 35 mm film produce a useful working standard which forms the basis of much of the decision making. Diapositives at 10 x offer essential technical information for making preliminary comparisons. These photographs should be made with the surface of the painting dry and also wetted with mineral spirit. Repeated visual observation at 30 x using a hand held magnifier provides a rapid and useful check. It should be stressed that visual observations at 10 x - 30 x magnification are easily made and should accompany each stage of the operation. We use an illuminated magnifier run on small batteries. It provides the most useful and rapid way of following progress.

### The Basic Requirements for the Successful Use of Micro-Friction Method

The method can only be used safely if the structure of the original painting meets the following conditions:

1. The paint must be fully cohesive and without structural weakness e.g. flaking, cupping, powdering or fissures within the paint layers, but a normal crackle pattern offers no problems.
2. The original paint layers should have some resilience and a degree of elastic recovery.
3. The support, if exposed, should be in a sound condition.
4. The unwanted surface coatings, glues, resins, etc. must be harder and more brittle than the original paint layers and support.

If any of these conditions is not met the use of the micro-friction method could be harmful to the painting, and other means of cleaning should be sought.

Using the air pencil and a suitable abrasive powder and pressure, layers of lining paste or isolating layers of glair (white of egg) or animal glue, size, resin varnish, dirt, grime can be removed collectively in a single operation. A more common practice however, is to remove these layers in stages, gradually reducing their thickness until a stage is reached when the colour of the original paint begins to appear. There are occasions when the removal by friction of the upper layers of varnish and deposits is used as a preliminary for the application of solvents.

In cases where the original paint layers have been mixed by the artist with varnish during painting both methods have been found to be valuable. Finding layers of oil paint retouching, over the original tempera and gesso on Gothic polychrome figures is not uncommon, and in this case the micro-friction method can remove the oil paint without affecting the original paint and gesso layers. This dry process also prevents any staining of the paint and gesso by discoloured solvents.

A particular advantage of the method is the means of separating individual layers of varnish, giving the conservator the opportunity of keeping the earlier layers intact, when this is desirable.

### Equipment

The micro-friction method requires the following facilities:

1. A fully sealed ventilation chamber with a large glass observation window and hand holes (see photo No. 1). The chamber should be large enough to house an average sized painting.
2. A strong dust-filter system fitted beneath the chamber.
3. A compressor with an adequate air storage cylinder and air pressure control. Compressed CO<sup>2</sup> or N<sup>2</sup> in cylinders can also be used.
4. An air abrasive unit having a foot control. Sandmaster, Ultra-fine Sandblaster (Type FG 3-82, access to three powders).
5. A range of air pencils of varying nozzle sizes. 0.4 mm, 0.6 mm, 0.8 mm, 1.2 mm and 1.8 mm.
6. A range of selected abrasive powders. Glass beads (A.Q. 0-50 mu, GP 44-88 mu), aluminium oxide (Biloxit No. 220 44-74 mu, No. 280

- 37 mu, No. 360 23 mu, No. 500 13 mu).
7. A cool directional light source placed within the chamber.
  8. A high intensity spotlight placed outside the chamber.
  9. Magnifiers of 10 x to 30 x magnification (Lascaux 30x FF-393)

The choice of the equipment depends largely on the particular requirements of the conservator and the type and size of paintings normally dealt with. Conservators using this method for the first time should systematically experiment with various paint/support combinations, preferably not on original paintings. They will find that by varying the abrasives, the volume, the nozzle size and the pressure used that they will be able to remove a wide variety of materials, e.g. printing ink or graphite lines from paper or grime deposits from fabric. Experience is built up which leads to finer and more exact control when handling Old Master paintings and modern and contemporary works.

#### Technique

Use an air abrasive pencil with a fine nozzle aperture size and test a very small area on the edge of the painting. Move the pencil evenly from a distance (20 cm) and draw it downwards in an action similar to shading with an aerograph spray pencil. The small area covered is then lightly brushed to remove the whitish residues of fractured varnish, and observed carefully under magnification of from 10 x to 30 x using a simple hand-held magnifier. The surface at this stage will still show the powdered remains of the old unwanted surface coatings. This gives the conservator an opportunity to assess the quantity of the components.

In very thinly painted areas, the edges of the strokes should be studied closely and spot tests made; these minute areas can be examined after successive treatments. Thus the operation should not be made as one single action, but as a first and second and third, usually final, cleaning stage. Spot tests enable the correct distance and larger movement of the pencil to have the same safety factor. The work is halted from time to time for the removal of residues and the surface examined for possible structural weakness. A stage is soon reached when the appearance of the surface grows richer and more colourful. Some paint layers respond well and show attractive tempera-like surfaces with considerable sheen and depth of colour. Gentle wiping with mineral spirit removes the last trace of the whitish powdered deposits and the paint qualities can be seen once again close to their original state. Some paintings do not need to be varnished and have satisfactory and pleasing surfaces.

The final stages of cleaning can be critical and call for sensitivity and an evenness of touch on the part of the conservator. The angle of the pencil is often slanted to enable surface deposits to be blown aside obliquely. The pressure can now be reduced by moving the air pencil further away from the painting - strokes of the pencil become wider. The actions are in many respects similar to those of spraying varnish but of course covering an operation on a very much smaller scale.

#### Choice of Abrasives

There is a wide range of air abrasives of various types and hardness. Some have resilience and unusual properties of elasticity such as the glass powders (rounded spheres); others are as soft as powdered rubber. Some of the most usual abrasives used on painted surfaces are, glass beads A.Q. (0-50 mu and GP 44-88 mu) and aluminium oxide, Biloxit, powders (see "Equipment").

All abrasive materials used should be of regular and even particle size. Most abrasive powders are sold with a stated range of average particle size. This is an important factor and care should be taken in the choice of the type used according to the stated specifications of the manufacturers. Abrasive powders should be kept very dry, as dampness hinders the even flow of the abrasive through the air pencil.

The type of "friction pattern" set up by the abrasive powder plays an important part in the ease of fracturing the surface of the coating.

The action of micro-friction is concerned with gently cracking and splitting the unwanted material from the original surface, allowing the fractured scales to be swept away in the air flow. Splitting, rather than abrasion, is the aim. If the abrasive should penetrate



larged detail of a tinted  
pasto (Claude Monet).  
tual size 3 mm high, ca.  
x magnification, before  
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ite lead/zinc white in oil  
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all dark particles of pig-  
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etween the varnish layers.

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cent varnish layers have  
en removed, but fragmented  
sidues of earlier dark  
rnish still remain in the  
int hollows (RHS). The form  
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dicating some original  
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en seen under similar mag-  
fication ca. 80x.









the surface it would be most detrimental to the paint. Too high a pressure or wrong choice of abrasive will cause this to happen. The particle shape and its degree of elasticity is particularly important.

The abrasive powder is vibrated in the pressure container and passed through a sieve plate into a stream of regulated compressed air in the air hose, and thus to the air pencil. The volume of the abrasive powder passing through the pencil is controlled separately.

An electrical magnet controls the amount of vibration and serves to regulate the volume of abrasive used. The pressure reducing valve regulates the air pressure at the pencil, and this can be read on a built in manometer.

In practice one adjusts the air pressure and the abrasive output with the volume regulator to obtain the optimum working conditions. Starting at low volume and gradually raising the pressure or volume until the desired flow of abrasive is obtained. Effective control depends on the air pressure, volume of abrasive, and the working distance of pencil to painted surface, these can vary widely irrespective of the kind of abrasive used.

Of course the choice of air pressure used is related to the type of powder selected. Too high a pressure will impair a delicate surface but the same pressure might be suited to the removal of a heavier material.

Oil paints of any age vary widely in plasticity and elastic recovery, but it is clear that those with a "normal" resilience can be treated with air abrasive micro-friction methods without any loss of form or colour. Indeed, in place of loss, the very opposite is true when the method is used with expertise. The original colour not only returns but becomes an inherent part of the form of the paint; many paintings seem to exhibit vital plastic values of a kind quite unlike those which are found on a painted surface that has been treated with solvents.

But why should there be such differences? We believe there are several good reasons, including the more even removal of the darkened surface layers. The fine abrasives can reach into the hidden cavities and folds of the paint structure almost as quickly as into the more open surface of the paint. The lack of residual staining by contaminated cleaning solvents and the lack of swelling and leaching of the original paint layers must also play a part. Time and research will tell us more precisely why these differences occur.

The micro-friction method is particularly suited to the treatment of Impressionist pictures, and we have had significant success in treating works by Renoir (thin rubbed glazes with abrupt raised impastos), Monet (overlapping impastos) or Utrillo (surface textures with lean over-pigmented paints and mixed media) and many other painters of this period. The method can be adapted to suit a wide range of structural problems connected with paintings in tempera, oil, alkyd and acrylic paints.

This means of removing insoluble layers of glue and varnish presents many new opportunities for conservators dealing with paintings. We gave a demonstration of this method in the Tretyakov Gallery in Moscow in 1986 and we were able to show the practical possibilities of recovering the original appearance of an eighteenth century portrait which had previously resisted all attempts at "cleaning" and had been relegated to become "guinea-pig". This portrait was almost totally obscured by numerous layers of glue and darkened varnish and grime. Yet, these dark and very opaque layers were quickly and easily removed with the air pencil and the original was revealed again in its fresh and undamaged state. The picture, when damped with mineral spirit, regained its former colour contrast and vitality. The operation was rapid and effective because the surface materials fractured collectively, allowing the painting, which was quite resilient, to show once again its colour and form.

Another successful treatment was the removal of an aerosol spray lacquer from a portrait by Varlin, the Swiss painter. In this case, a vandal had sprayed black paint onto the features of the head, obliterating the eyes, nose and mouth. The structure of the original painting, (oil paint onto unprimed open-weave jute canvas with irregular raised impastos) would have created problems if solvents had been used, for these would have gone into both the canvas and the weakly bound paint layers and inevitably stained both. The micro-friction method using the air pencil, starting from the edge and working towards the centre of the damage, removed all traces of the black lacquer from the original. The original colouration and

the complex structure of paint and canvas were fully recovered and showed no trace of the previous damage.

#### Conclusion

The micro-friction method is versatile and can, in experienced hands, produce results unobtainable using solvent methods of cleaning. Paintings so treated retain much of their vitality of surface and are free from discolouration by residual varnish or abrasion by rubbing. The hollows of the paint are as clean as the uppermost surface. The original structural qualities of the painting are fully recovered, but the method is not a universal one and can only be used within a strict range of conditions. However, if these are met the results can exceed those of other cleaning methods.

It must be emphasised that the micro-friction method can be destructive but we recognize that all methods can be destructive if misunderstood or misused. In justification of the use of micro-friction we can only repeat that no trace of paint ever need be lost or impaired, if the method is used correctly. Judged as an alternative means of cleaning it opens up new avenues and has, we believe, a future potential in conservation, offering means of recovery for many pictures previously judged as being beyond hope.

We would like to thank Mr. Alois K. Diethelm, of Lascaux Restaurauro for once again helping us with our research and providing essential advice and equipment furthering the application of micro-friction to the conservation of paintings. Conservators wishing more information on methods or equipment should write directly to him at Lascaux Farbenfabrik, Dept. Restaurauro, CH-8306 Brüttisellen/Switzerland.



## SUMMARY

The Fine Arts Laboratory and Scientific Services at the Canadian Conservation Institute have initiated a project to investigate alternatives available for the lining of paintings. The goal of the project is the identification of a range of suitable lining support systems, with defined physical and mechanical properties, which will minimize stress development in a painting.

The project is divided into 4 stages: Mechanical Testing of Model Paintings; Peel Testing of Lining Adhesives; Testing of the Mechanical Properties of Lining Supports; and Testing of Lined-Model Paintings.

The first phase of the project is nearing completion. The prepared samples include combinations of linen canvas, glue size, oil and acrylic grounds and oil paint. The samples are mounted in uniaxial restraining devices which permit measurement of stress relaxation over the long term, stress with applied strain and stress as a function of Relative Humidity (RH). Measurements also included weight change and free-hanging dimensional change in response to change in RH.

Notable results to date are the following:

In samples prepared as Model Paintings, there is a dramatic increase in stress at low RH and a loss in stress at moderately high RH.

Stress relaxation may follow a simple equation that might permit prediction of eventual stress in a sample from values obtained in the first five minutes after strain is applied. A wide variation in the speed of response of the different sample types was noted.

Following a change in ambient RH, the maximum response of the samples, in weight and dimension, occurred within approximately 1 - 3 1/2 hours.

## METHODOLOGY AND STATUS OF THE LINING PROJECT, CCI

Debra Daly

Conservator, Fine Arts and Polychromes Laboratory  
Canadian Conservation Institute  
1030 Innes Rd., Ottawa, Ontario, Canada, K1A 0M8

Stefan Michalski

Conservation Scientist, Environment and Deterioration Research  
Canadian Conservation Institute

## INTRODUCTION

In recent years there has been a change in approach to the structural restoration of fabric supported paintings. This is due to a re-assessment of the suitability and performance of traditional lining materials and methods and to increased knowledge of the mechanical behaviour of paintings. Conservators are now investigating methods of preventive conservation and treatment which minimize stress development in a painting without lining. As well, a re-evaluation of lining systems is in progress. As old materials and methods are partially discredited and new ones are adopted for use, the conservator is confronted with lining alternatives which vary in properties of stiffness, rigidity and bond strength, and which have not yet withstood the test of time. To assist in the choice of an appropriate lining system, a comparative study of the mechanical properties of lining supports and adhesives and their ability to minimize defects in a painting is required.

The Fine Art Division and Conservation Research Services at CCI have therefore initiated a project on Lining Supports and Lining Adhesives. The experimental procedure will also allow analysis, by CCI and others, of other materials as they become available.

**PURPOSE:** The project will characterize the physical and mechanical properties, over the short and long term, of a range of current lining support systems.

**METHODOLOGY:** The methodology is based upon simulation testing involving the use of restrained samples prepared as model paintings, lining supports and lined-model paintings, which are known to develop high stress as a result of extreme environmental conditions.

Initially, all tests will be undertaken upon uniaxial samples, prepared as outlined in ASTM D1682, with slight modification as required by the testing apparatus. Eventually a reduced number of samples will be tested in the biaxial format.

The basic apparatus is a restraining jig which allows observation of the short and long term behaviour of the samples with provision for applied strain and the recording of stress. Other samples will be free-hanging.

Some tests will be performed only once. Others will be repeated upon another set of samples after a period of natural ageing.

The following properties will be measured: Stress Relaxation, Creep, Elastic Recovery, Modulus of Elasticity, Elongation, and Bond Strength.

The materials to be tested will be representative of those in use by practicing Fine Art conservators. Screening will continue as data is accumulated.

The project is divided into 4 stages:

**1 The Testing of Model Paintings:** Further clarification of the nature and magnitude of harmful force development in paintings is necessary to identify and assess the performance requirements of lining support systems. Quantitative and qualitative analysis of stress development will be undertaken on samples prepared as Model Paintings. The stress and related defects will result from: 1) the mechanical behaviour of the component layers of a traditional painting on fabric; 2) applied strain; and 3) exposure to extreme environmental conditions. The simulation testing may demonstrate phenomena that are unpredictable or too complex to isolate with present knowledge. The testing will also result in refinement of the general testing method.

The Model Paintings to be used in the tests are of two different types. (Fig. 1) Model Paintings Type 1 are based upon the structure of a traditional painting on fabric (similar to that used in the first testing stage described below). Model Paintings Type 2 will be prepared with isolated areas of

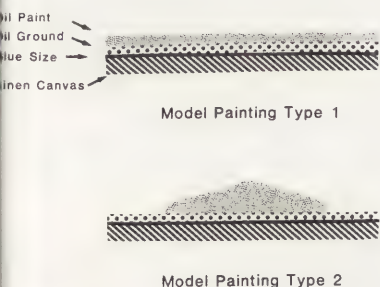


Fig. 1: Model Paintings

impasto. The behaviour of the samples, restrained under various conditions of stretching and lining, will be observed under the test conditions of fluctuating RH and Temperature (T).

This testing stage is nearly complete and is described more fully below.

**2 The Bond Strength of Lining Adhesives :** Peel testing will measure the bond strength achieved with various lining methods, adhesives and supports. Samples will be prepared as outlined in ASTM D 903, using linen as the flexible member. Peel strength will be measured at two speeds using an Instron Tensile Tester, Model 4201.

Impregnating adhesives, non-impregnating adhesives and pressure sensitive adhesives will be tested. Sample preparation will include a range of variables associated with the application and activation of the adhesives. Whenever possible, the data will be correlated with research undertaken by colleagues elsewhere such as that reported by Phenix and Hedley on pressure sensitive adhesives<sup>1</sup>.

Characterization of the chemical and physical properties of the adhesives will be undertaken in the Adhesive Testing Programme at CCI, co-ordinated by Jane Down<sup>2</sup>.

**3 The Mechanical Properties of Lining Supports:** The recent focus upon performance requirements of lining supports has resulted in an active search for more suitable materials. High stiffness lining supports such as fiberglass, polyester and various semi-rigid supports, have largely replaced linen as a lining fabric. As Hedley pointed out, the particular mechanical properties we are looking for in these fabrics are: tautness under minimal applied elongation, for example, high stiffness; resistance to stress relaxation and creep; and isotropic behaviour<sup>3</sup>. In terms of these mechanical properties, rigid panels may be the most effective way to minimize stress in a painting, but the marouflage procedure may not be acceptable or advisable for all paintings from the point of view of reversibility, aesthetics and lack of flexural qualities.

Linen and a variety of fiberglass and polyester fabrics will be investigated. Various stiff and semi-rigid support laminates will also be included.

Literature values on the mechanical properties of a single ply of each fabric will be compiled, though scant comparative data is available. Measurement of the mechanical properties of lining supports, both single and laminated, will be undertaken at conditions known to affect force development in paintings.

**4 The Testing of Lined-Model Paintings:** Testing will culminate in simulation of the performance of lined paintings in response to either constant strain, applied strain or extreme environmental conditions. The objective is to assess the ability of the lining materials and methods to minimize further defects in a painting. Verification of the results of uniaxial testing will be undertaken on a few sample types in the biaxial format.

By lining Model Paintings Type 1 and Type 2 upon supports representing a range of rigidities and by using lining adhesives of various strengths, the forces involved in the creation of defects can be deduced. (Fig. 2) These samples may clarify the magnitude of force associated with out-of-plane displacement, or what Mecklenburg refers to as "force realignment", at tears and in areas of heavy impasto<sup>4</sup>. For example, to what extent is out-of-plane deformation considered a failure, or to what extent is it to be tolerated as a stress release mechanism in lieu of cracking? Interpretation of the results will provide information on the in-plane stiffness and flexural qualities required of the lining supports, on the ability of the adhesive bond to resist failure and on the ability of the lining systems to maintain their properties over time and under fluctuating environmental conditions.

#### TESTING OF MODEL PAINTINGS:

Over the past two years, sample preparation and mechanical testing of the Model Paintings Type 1 have been undertaken.

#### SAMPLE PREPARATION:

After consulting many artists' manuals, it was decided to represent the 'typical' painting by samples prepared with linen canvas, rabbit skin glue (RSG) size, white lead in oil ground and a common pigment, lead white, in linseed oil.

Unwashed linen canvas was stretched upon a Lebron type stretcher so that the tension could be altered as required. All canvases were brought to an equal degree of tautness using a tautness tester. The tautness tester is a dial

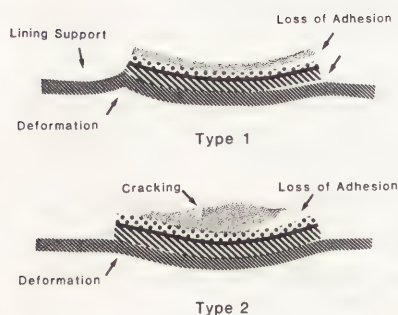


Fig. 2: Model Paintings  
Anticipated Modes of Failure



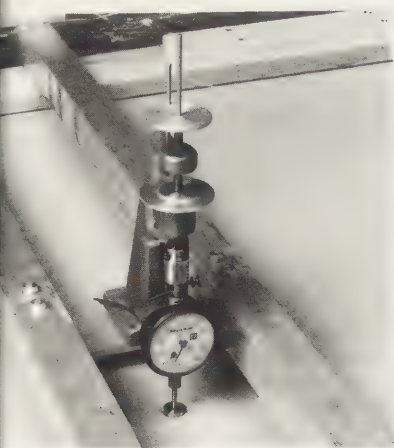


Fig. 3: Tautness Tester

caliper, secured to a metal framework. With the instrument placed across the canvas, supported on the stretcher bars, the displacement of the fabric under a 5 gram weight was measured. (Fig. 3) The exposed expansion bolt allowed adjustment of the tension as required.

Four main sample groups were prepared:

- (1) Fabric (Unwashed linen)
- (2) Fabric + Size (4% RSG applied with a brush)
- (3) Fabric + Size + Ground (Two brush coats; Frederix Oil Priming)
- (4) Fabric + Size + Ground + Paint (One brush coat Grumbacher white lead in linseed oil; applied 1 month later)

Comparison of the mechanical properties of these four sample types allows observation of the influence of each successive layer on the behaviour of the painting as a whole.

In addition, because of the diversity of opinion in the artists' literature on a recommended ground application, the following samples were also prepared.

- (5) Fabric + Size (4% RSG gel, scraped on with a metal spatula)
- (6) Fabric + Size (brush) + Chalk/Glue Ground
- (7) Fabric + Size (brush) + Emulsion or Half-Chalk Ground  
(2:1 glue size/linseed oil)
- (8) Fabric + Acrylic Ground (commercial)

Sample strips 2.5cm wide, 20 cm in length, were cut from prepared canvases. Most samples for the stress and free-hanging tests were cut along each of the warp, weft and bias directions. Several samples (2.5cm x 2.5cm) were also cut for the weight measurements.

Testing commenced nine - eleven months after sample preparation. In other words, testing was undertaken on relatively young samples.

#### MECHANICAL TESTING EQUIPMENT:

The testing equipment is divided into 4 parts:

- 1) Environmentally Controlled Cases : Three cases were constructed to allow testing within an environment which was maintained at a specified RH. The main testing case was constructed to enable the operator to manipulate the samples and equipment without affecting the environment in the case. Two additional cases were built which controlled and maintained the relative humidity (RH) within the testing case. Using saturated salts and silica gel, the RH was maintained at 20% in one case and 72% in the other.

To calculate the Equilibrium Moisture Content (EMC) of the samples testing at 0% RH was required. An environment of 2 - 6% RH was achieved with the mechanical environmental testing chamber connected to the testing case. However, the air currents created by the heating and cooling cycles of the large chamber interfered with the weight measurements. In later testing, weight change measurements were repeated on a few samples in a passive chamber desiccated with calcium chloride.

- 2) Weight Change Apparatus : Samples (2.5cm x 2.5cm), were hung in the testing case and weighed within the testing environment. (Fig. 4) The operator manipulated the samples using a metal hook through a small hole in the case exterior. The weight was monitored after a sudden change in RH.

In general, the system worked well except for the problem of the air currents created by the fans when returning the case to 50% RH. The breezes interfered with obtaining a true weight measurement. Modification of the procedure will be required in future tests.

- 3) Free Hanging Apparatus : Strips from each sample group were hung from a metal frame inside the testing case. Glass slides adhered to the bottom of the sample carried a small photographic scale. (Fig. 5) Using a microscope the change in length of the samples was read as the scale moved past a metal straight edge.

This simple apparatus worked well, although the dimensional change occurred much faster than expected. As a result, only two samples could be monitored during a rapid change in RH.

Fig. 4: Weight Change Apparatus  
(Passive desiccation chamber)

Fig. 5: Free-Hanging Apparatus

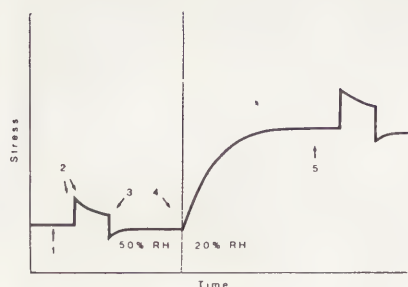


Fig. 6: Test Sequence for Raw Data

- 1 Stress at %RH
- 2 Strain and resulting stress relaxation
- 3 Strain removed
- 4 Change in %RH
- 5 Stress at new %RH

4) Stress Measurements (Restraining Frames) : The samples were installed in the restraining frames with a 1 mil strain. One sample of each type was also installed with a 2 mil strain. Figure 6 shows the sequence of stimuli used to collect the data for the stress measurements.

Restraining Frames and Measuring Apparatus: (Fig. 7) Two clamps, held approximately 20 cm apart, are placed at the ends of a square metal tube. The sample is held at a fixed distance between the two clamps. One clamp is mobile but is held in place against a metal pin. This clamp can be pulled to strain the sample slightly. When placed in the measuring apparatus, an acrylic plate connects the mobile clamp with a load cell. By turning a threaded rod, the load cell is pulled until the clamp is just taken off the pin. This "break contact" point is monitored by an electrical resistance meter. At this point the load cell is measuring the force in grams that just balances (or describes) the force in the sample.

A strain gauge is also attached to the measuring apparatus to record the displacement in the sample when the incremental strain is applied. Improvements in the system can be made. The peak stress resulting from applied strain is dependent upon the rate at which the strain is introduced. Modifications should be made so that both the rate and the strain applied are constant from one sample to another.

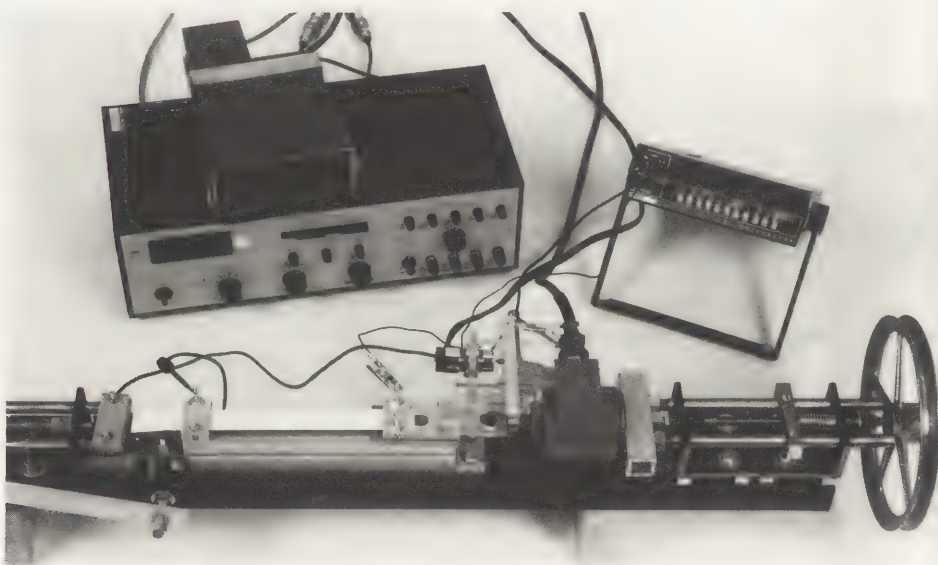


Fig. 7: Restraining Frame and Measuring Apparatus

#### ANALYSIS OF THE RESULTS:

A Hewlett Packard Series 200 Computer is being used with appropriate software. Interim results are presented below.

#### STRESS MEASUREMENTS:

The stress in each sample was measured three days after a change in the environmental conditions. The sequence of change was as follows: 1) 43% - 20%RH; 2) 20% - 48%RH; 3) 47% - 71% RH; 4) 72% - 43% RH; 5) 33% - 4% RH; 6) Final reading at 47% RH. The stress values obtained at each RH are plotted in the following graphs.

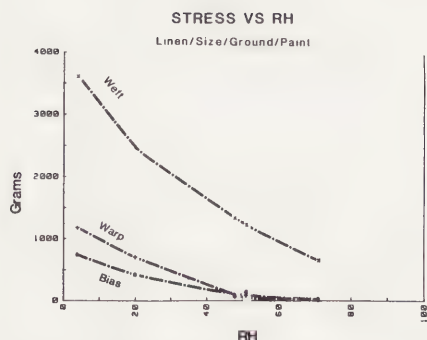


Fig. 8: STRESS VS RH (Linen/Size/Ground/Paint)

Fig. 8 compares the stress vs RH of the sample composed of linen, size, ground, and paint in the warp, weft, and bias directions. At 50% RH there is 1 kg of force in the weft sample and almost 0 in the warp and bias. This is 1 kg of force across a 2.5 cm wide sample. The equivalent force across a metre wide painting would be 40 times this value.

Consistent with previous data from Mecklenburg's studies, there is a dramatic increase in stress at low RH and a loss of stress in the painting at a moderately high RH. Also interesting is the extreme stress obtained at 4%RH.



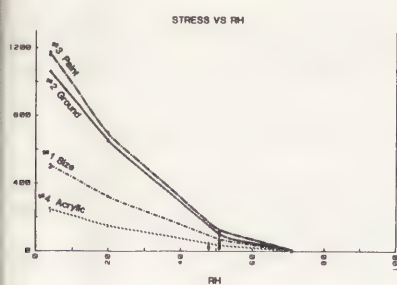


Fig. 9: STRESS VS RH Warp direction

- #1 Linen + Size
- #2 Linen + Size + Ground
- #3 Linen + Size + Ground + Paint
- #4 Linen + Acrylic Ground

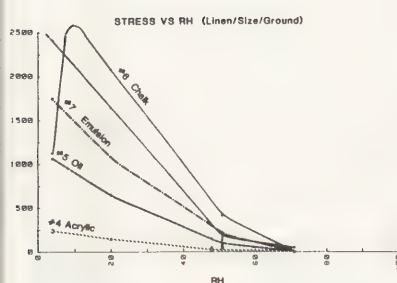


Fig. 10: STRESS VS RH (Linen/Size/Ground)

- #4 Linen + Acrylic Ground
- #5 Linen + Size + Oil Ground
- #6 Linen + Size + Chalk/Glue Ground
- #7 Linen + Size + Emulsion Ground

Fig. 9 compares the stress development in different sample types, all in the warp direction. Again, the data reveals an increase in stress at low RH and a decrease at moderately high RH. (In these samples, installed with 1 mil strain, the stress completely dropped out at 71%. The point at which the stress drops out is not apparent in our procedure and will vary according to the initial stress in the sample.) The addition of the paint layer has only resulted in a small stress increase over that in the sample with size and ground. The paint film however, was still very young (1 year).

Certainly, in comparison to the samples with an oil ground and oil paint layers applied, the sample with the acrylic ground does not develop nearly the stress at any relative humidity tested. In fact, in the worst situation it develops only half the stress that the canvas/size sample develops.

Comparison of the behaviour of the different grounds in Fig. 10, reveals similar trends, but there are significant differences in behaviour. Not surprisingly, the brittle chalk ground develops the highest stress. This graph compares the behaviour of two chalk ground samples. In one, the chalk ground cracked just as the sample was slightly strained. The reduced stress illustrates the stress release caused by a crack; the stress at 4% is now 1.1 kg whereas if the crack had not formed, the stress may have been up to 3 kg.

#### FREE-HANGING SAMPLES; DIMENSIONAL CHANGE:

The free hanging samples allowed observation of the dimensional change as a function of RH and time.

In Figs. 11 - 13, the % change in length vs RH has been plotted. The length at the start of the cycle, 43% RH, as been used as the reference length.

Fig. 11 shows the behaviour of the Linen + Size sample in the warp, weft, and bias directions. The warp sample shows the greatest movement; shrinking up to 1.5% at 4% RH and expanding 0.25% over the sample length at 71% RH. Note also that there was a 0.75% decrease in length when the final reading was made at 50% RH. In comparison, the bias moved less and the weft moved only slightly.

Fig. 12 compares the behaviour of the different sample types, all in the warp direction. The Linen + Size sample moved to the greatest extent. The behaviour of the other sample types are quite similar to each other; at 71% RH a 0.25% expansion was observed and a 0.5% contraction was observed in low RH. This contraction represents 0.5 cm movement across a metre-wide painting. Note that 1 mil has been marked on the y axis. During installation of the samples in the restraining frames, even the 1 mil strain produced large forces. Certainly, in comparison, the free-hanging change in dimension due to RH is much larger than the initial applied strain and has the potential to cause extreme stress development.

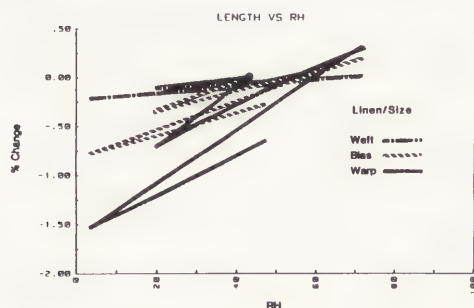


Fig. 11: LENGTH VS RH (Linen/Size)

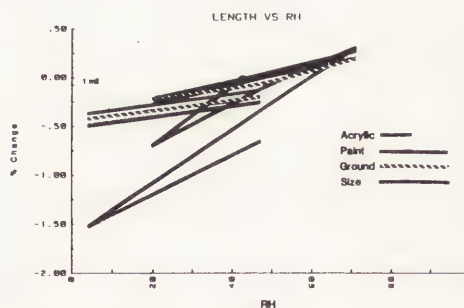


Fig. 12: LENGTH VS RH Warp direction

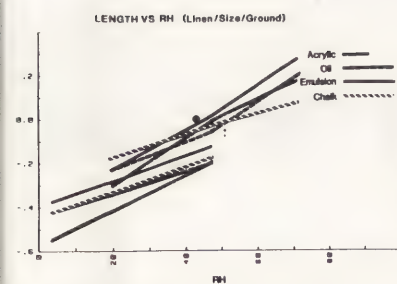


Fig. 13: LENGTH VS RH (Linen/Size/Ground)

Fig. 13 compares the different grounds. All the ground preparations are behaving in the same range as a typical painting sample, however slight differences are noted among the sample types. The acrylic sample expands more than the others at 71% RH, but does not seem to shrink as much at 4% RH. On the other hand the emulsion ground shrinks more than the others at 4% RH.

These trends were not completely reflected in the comparative stress values. (Fig. 10) The emulsion ground does not develop as high a stress as the chalk ground yet it shrinks more at low RH. Stress development in a painting at different RH is affected both by the change stiffness and by the change in dimension. With other data, not shown here, the modulus of elasticity of the samples can be calculated at each RH, giving a measure of their mechanical stiffness. Future analysis will allow discussion of the contribution that the change in modulus or stiffness has upon the resulting stress compared to the contribution of the dimensional change. In comparing the behaviour of the

different grounds, these factors appear different from one sample to another. Compilation of the data also suggests that stress relaxation is a major factor in the magnitude of stress development in a painting caused by environmental change.

The experiments also look at the behaviour of the samples over time.

In Fig. 14, the fraction of the total change in length is plotted against time. The data for the Linen + Size sample, which shows a significant change in dimension, is plotted. Of interest is the speed with which the sample responds to an environmental change. Half the change occurs within the first 5 minutes and the total change is approached after an hour.

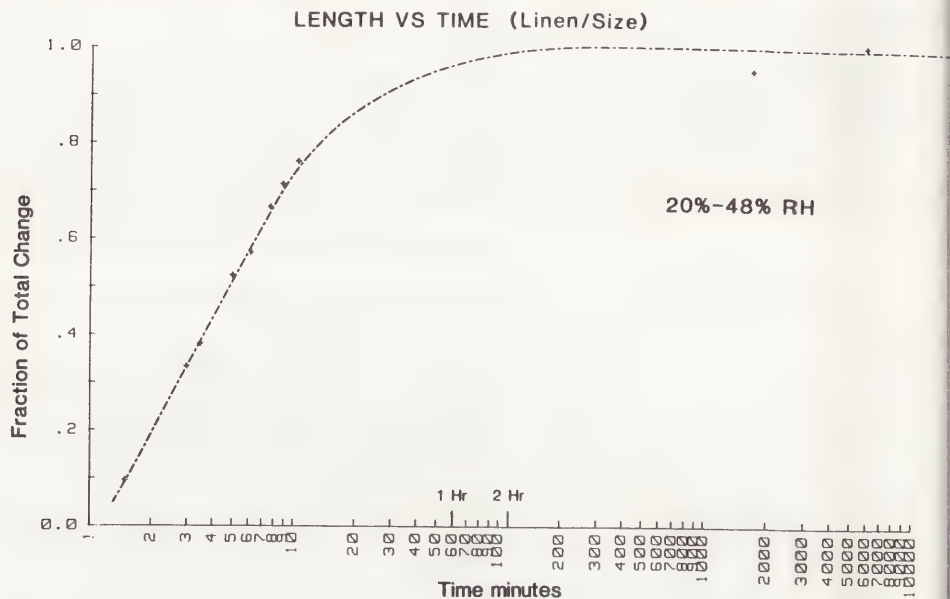


Fig. 14: LENGTH VS TIME (Linen/Size)  
20% - 48% RH

Fig. 15 compares the rate of dimensional change in the linen/size sample for the four RH changes made. The rate of change, is relatively fast and is not affected significantly by the direction of RH change. It follows that the response of paintings to even short, fast environmental changes will be fairly quick. Anything to slow down or eliminate fast RH changes close to the canvas will be beneficial in minimizing stress development in the painting.

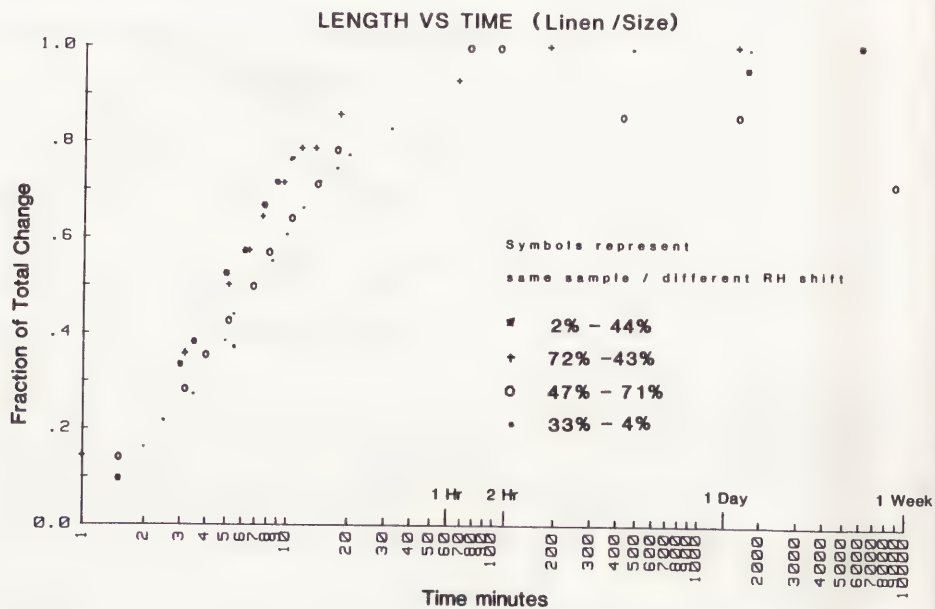


Fig. 15: LENGTH VS TIME (Linen/Size)



## WEIGHT CHANGE MEASUREMENTS:

The rate of absorption or desorption of moisture in the samples is shown in Fig. 16 - 17. Once again, the fraction of total weight change is plotted vs. time. Fig. 16 reveals that the weight change is occurring at much the same rate as the change in length of the samples.

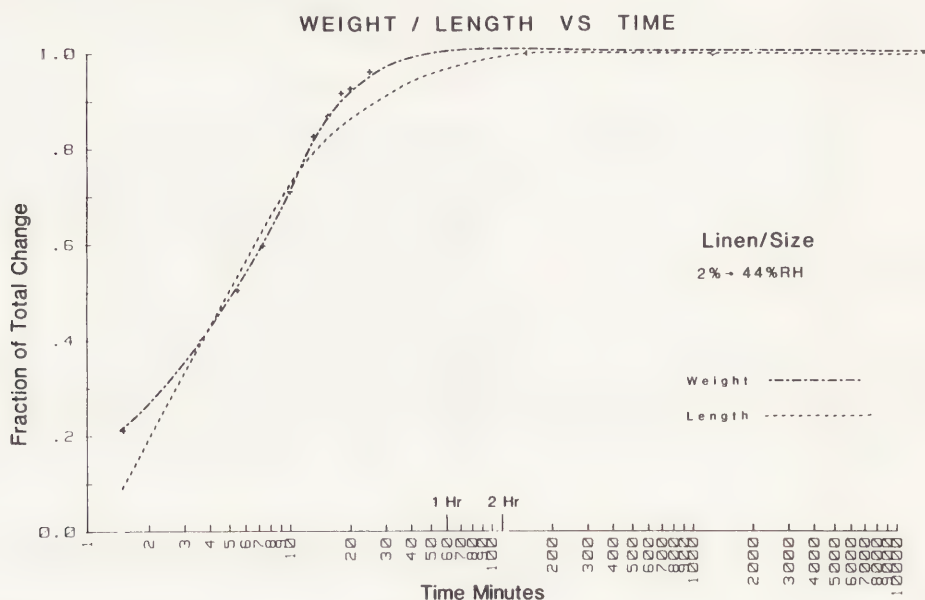


Fig. 16: WEIGHT AND LENGTH VS TIME (Linen/Size)  
2% - 44% RH

The weight data is disappointing due to the problems with air currents. Weight measurements obtained within a passive desiccation chamber or in ambient room conditions (outside the testing chamber) were successful. Graphs reveal a much smoother line. (Fig. 17)

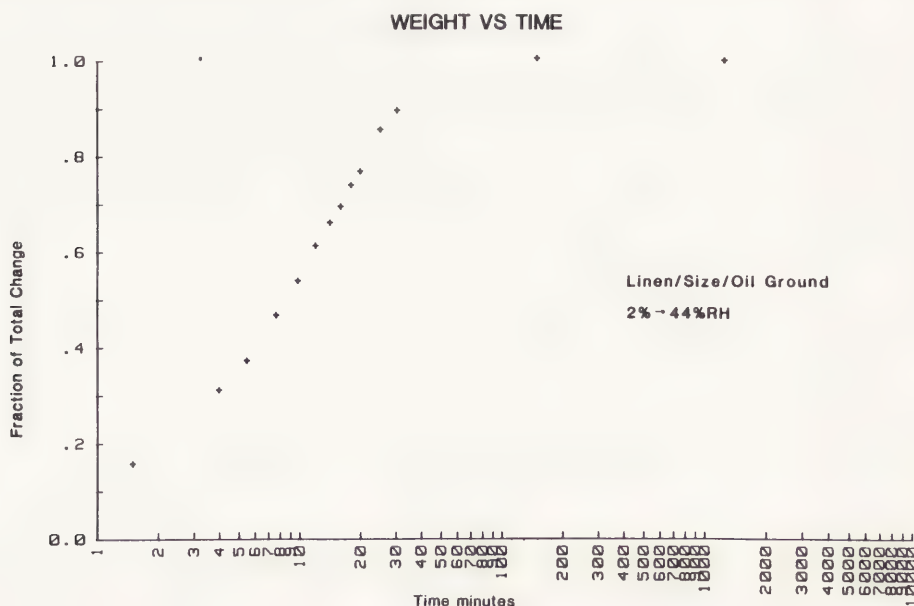


Fig. 17: WEIGHT VS TIME (Linen/Size/Oil Ground)  
2% - 44% RH in passive desiccation chamber

## STRESS RELAXATION:

Stress relaxation over the long term has been recorded for a few samples. It appears that the rate of stress relaxation follows a simple equation that might permit prediction of eventual stress in a sample from values obtained in the first five minutes after the strain is applied. Preliminary data reveals that stress relaxation, after strain is added to the sample, can be described by a simple equation that covers a very wide range of time - from ten seconds

to several weeks. It is of the form:

$$\text{Stress} = \text{Stress at one minute} \times \text{time (minutes)} \text{ to the power of } (-n)$$

This power law has been shown to fit stress relaxation in other plastic materials, with "n" typically near  $0.10^5$ . The values of "n" measured thus far vary between 0.02 and 0.07 depending on the paint media and RH. This range represents a wide variation in the speed of response, or stress relaxation, of the different samples. For example, the predicted time for half of the one minute stress to drop out varies between two billion years ( $n = .02$ ) and two weeks ( $n = .07$ ). The data to be collected at the one year interval will be crucial in establishing how long this power law holds.

"Zero time" stress does not exist as this requires strain to be added in an infinitely short period of time and would result in an infinitely high stress. The apparatus is limited to applying the stress in about one second. Shorter time periods are in the realm of impact and vibration phenomena, not natural RH and temperature changes. (Although important to paintings, the study of impact and vibration is not part of this project.)

It does appear that stress relaxation is playing a major role in determining the peak stress that results within a painting as it responds to natural RH changes. It is apparent that the stress values measured in the samples after an RH drop are much less than would be predicted by free-hanging dimensional changes. Under natural RH change some stress is dropping out as it is being created. In circumstances of rapid strain, such as vibration or impact, much higher values of stress would be reached and the likelihood of damage would be greater.

The analysis of the data collected in the testing of the Model Paintings, particularly the stress relaxation data, is still underway. It is anticipated that the final results will be presented at the conference.

#### REFERENCES :

1. Phenix, A., Hedley, G.; "Lining Without Heat or Moisture", ICOM Committee for Conservation Preprints, Vol. 1, (Copenhagen), International Council of Museums, Paris, 1984, pp. 84.2.38 - 84.2.44.
2. Down, J.L., "Adhesive Testing at the Canadian Conservation Institute, Past and Future", Adhesives and Consolidants, Preprints, (Paris), IIC, London, 1984, pp. 18 - 21.
3. Hedley, G., "The Stiffness of Lining Fabrics: Theoretical and Practical Considerations", ICOM Committee for Conservation, Preprints, Vol.1, (Ottawa), International Council of Museums, Paris, 1981, pp. 81/2/2-1 - 2-13.
4. Mecklenburg, M. F. "Some Aspects of the Mechanical Behavior of Fabric Supported Paintings", Research Report (Unpublished), Copyright 1982.
5. Williams, J.G., Stress Analysis of Polymers, 2nd Edition, Ellis Horwood Ltd., Chichester, Distributed by John Wiley and Sons Ltd., New York, 1980.



## SUMMARY

In 1929 the Canadian artist Frederick Stanley Haines painted a series of eight murals for the Canadian National Exhibition. Each section is 2.2 metres high by 6.1 metres wide. (Fig.1,2)

This article traces the history of the conservation of these eight works. The first treatment of three of the sections was carried out in 1979 by the Canadian Conservation Institute (C.C.I.) in Ottawa, Canada. Subsequent work on two more sections was done by Sandra Lawrence in Toronto, Canada in 1985.

The author was commissioned to conserve two more of the sections during 1986. In this paper she outlines her approach to the work, which involved the use of a custom-built low-pressure table.

This approach differed from the previous treatments and was chosen to avoid certain long-term effects of environmental stress against which the treatment by C.C.I. had eventually proved ineffective. In treating the many tears in the canvases, the author used a standard moisture treatment, but on a very large scale. A large low-pressure unit was used to apply atmospheric pressure evenly to the surface of the drying canvas.

In confronting the problem of treating a large-scale canvas, the author has found a solution that may be of value to other conservators in similar cases.

# THE CASE STUDY OF THE LOW-PRESSURE TREATMENT OF A LARGE-SCALE CANVAS MURAL PAINTING: "THE SETTLEMENT OF CANADA" by FREDERICK S. HAINES

Diane Falvey  
Fine Art Conservator  
Art Care Conservation Services  
65 Bloomfield Avenue  
Toronto, Ontario, Canada M4L 2G2

## Introduction

Frederick Stanley Haines (1879-1960) was a well-established Toronto artist. In 1929 he held the position of Curator at the Art Museum of Toronto (now the Art Gallery of Ontario) and was Commissioner of Fine Arts for the Canadian National Exhibition (C.N.E.), an industrial, agricultural and cultural fair in Toronto, Canada, founded in 1879. Later, in the 1930's at the C.N.E. gallery, Haines organized progressive exhibits of the avant-garde artists, Picasso and Dali,<sup>1</sup> as well as others.

It was in the grounds of the C.N.E., in the Arts and Crafts Building, built in 1912, that the mural "The Settlement of Canada" was installed. The eight sections of the mural were hung around the interior of an octagonal base of the building's large glass dome. It is significant that after almost fifty years of constant change in the design and function of the interior and after complete refurbishing, the mural still hangs in its original place, a unique example of architectural decor of the period.

The mural was executed in Haines studio by a team of Ontario College of Art students in 1929. His influence is evident in the subject matter of the painting. He was "known as a painter of cattle, horses and dogs as well as an interpreter of the Canadian landscape".<sup>2</sup> The heavily outlined figures stand in a highly stylized landscape painted with broad areas of flat colour. Each section is composed of oil medium on primed canvas stretched on a wooden strainer and measures 2.18 m. high by 6.1 m. long.

## Condition of The Mural

Over the decades, extreme climatic conditions in the unheated building and water leaking through the roof of the dome had caused severe deterioration in the mural. All sections had friable tacking margins which in some areas were completely detached from the strainer. This resulted in slack tension, causing planar distortion in all canvases as well as cracked paint layers. (Fig. 3)

Some, but not all, sections displayed an advanced intralaminar flaking of paint layers. This could be explained by the inconsistency of the students' painting technique. Also, the paint was mixed in large batches to ensure uniform tone and colour for all sections of the mural. The paint in these pots may have begun to polymerize by the time the later sections were executed, thus leading to poor cohesion and/or adhesion in the design layers.<sup>3</sup>

Most of the sections suffered major tears. Some had been previously repaired and patched by C.N.E. personnel using old painted banners and polyester resin. Other tears, not repaired, had allowed shrinkage and major planar distortion in the canvas to occur in the area around the tear. (Fig. 4, 5)

The paintings were not varnished, but had an overall application of wax which protected the paint surface, particularly from water damage. The surfaces, front and reverse, were extremely dirty, with soot, grime, tar, water stains, bird excretions, etc.

With renovations and improvements to the building, especially the roof of the dome, the decision was taken to conserve the mural.

## Conservation History

In 1986, when the author was requested by the C.N.E. to treat two sections of the mural, five sections of the eight had been treated already.

Three of these sections were conserved at the Canadian Conservation Institute (C.C.I.), in Ottawa, Canada in 1978-79. In those three sections, the flaking paint was consolidated locally with Plexisol P550<sup>a</sup>. The surface was cleaned. Tears and punctures were repaired with inserts of linen held in place with Plexitol B500<sup>b</sup> and reinforced with narrow patches of Stabiltex<sup>c</sup> attached with BEVA adhesive<sup>d</sup>. The paintings were strip-lined with linen using BEVA adhesive. The original strainers were reinforced with Gatorboard<sup>e</sup> panels and a Pecap polyester monofilament<sup>f</sup> stretched over the panel as interleaf, before the painting was remounted.

The other two sections were treated by Sandra Lawrence's Studio in 1985. A full BEVA adhesive heat-set lining was attempted, but the lining fabric, Typar 9, was distorted badly with the application of heat and the lining was removed. Instead, the paintings were strip-lined, using a polyester/cotton blend fabric heat-set with BEVA. Polyester inserts and Reemay<sup>h</sup> polyester non-woven patches



Fig. 1: Disembarkation



Fig. 2: Buffalo Hunt



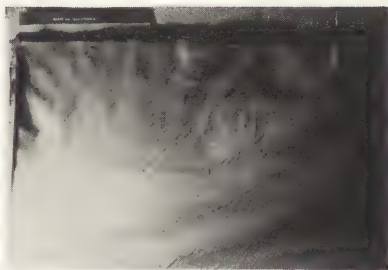


Fig. 3: Buffalo Hunt, detail, front, upper left corner

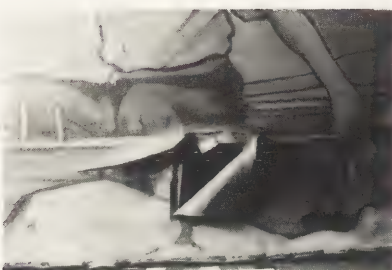


Fig. 4: Disembarkation, detail, front, large tear in boat area, before treatment



Fig. 5: Disembarkation, detail, reverse, small tear in centre of lower edge

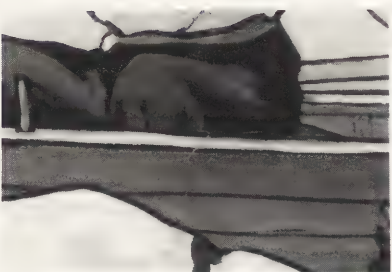


Fig. 6: Tear detail (Fig. 4), after treatment, before inpainting

were heat set with BEVA. Flaking paint was consolidated with Rhoplex AC634<sup>1</sup>. The paintings were cleaned and stretched onto new strainers reinforced with Gatorboard panel with a Tyvar interleaf. A varnish of Acryloid B72<sup>2</sup> in Cyclosol<sup>3</sup> was applied with a brush. This caused large areas of unconsolidated paint on one of the sections to curl up, needing further local consolidation with Rhoplex adhesive.

#### First Aid Measures

The author's inspection of the mural in 1986 revealed that some problems had developed in the three sections treated by C.C.I. First, the repaired tears had released from their narrow patches and the bond holding the tears together had failed. The tears had 2 cm gaps that had opened, due to shrinkage in the canvas horizontally along the warp direction. Secondly, active flaking in the paint layer was occurring. Previously consolidated areas were affected as well as areas not previously treated.

First aid treatment was carried out by the author. Dry BEVA was introduced behind the tears and the canvas was heat-set to the Pecap interleaf. The canvas is being held in this way until more extensive treatment can be carried out. Flaking paint was locally consolidated by wetting under the flake with iso-propyl alcohol and by running dilute Rhoplex AC 634 in water under the flake. When dry, the flake was heat-set into place.

Much was learned from the reaction of the previously conserved sections to seven years in the building's environment. The author concluded that the first treatment had not been sufficient to counteract the effect of the building's fluctuating climatic conditions. However, improvements in the method and materials could be made, which could make the subsequent conservation of the untreated sections more effective.

#### Case History

The most recent conservation of two previously untreated sections of the mural was carried out in 1986 by the author and a team of conservators. The major problems were threefold.

1. The realignment of the shrunken, torn canvas.
2. Treatment of bridging tears.
3. Overall consolidation of the paint layer.

The large span of the canvas and stress of movement during environmental cycles in the unheated building meant that the bond needed across the tear had to be strong. Also, the tension in areas of shrunken canvas had to be released. During treatment, with the realignment of major tears, planar distortion in the canvas occurred. By moisture treatment on a Dutch Stretcher, the canvas was relaxed, stretched and flattened, returning it to its original alignment and releasing tension in the shrunken areas. (Fig. 6) A source of even pressure over the entire surface of the painting was necessary during drying. Atmospheric pressure was used by extracting air from under the painting and creating negative pressure. For this purpose, a large, simple extraction unit was constructed with locally available materials.

The process for treating the two sections of the mural was as follows:

#### Pre-Consolidation

Before cleaning, all fragile and active flaking paint was consolidated. An application of dilute BEVA in Xylene was run under the flake and heat-set after 24 hours of drying.

#### Cleaning

The heavy grime, accretions and wax layer was removed from the surface with Vulpex<sup>4</sup>, dilute 10% in white spirit, emulsified to a gel with a small amount of ammonium hydroxide (NH<sub>4</sub>OH) in water. This was followed by many rinses of white spirit to remove all the residue. Overpaint was softened with Vulpex, then removed mechanically with a scalpel.

#### Facing

A facing of Eltoline tissue<sup>5</sup> was applied using rabbit-skin glue only to areas of fragile paint and around the edge of tears.

#### Preparation For The Dutch Stretcher

The painting was removed from the original strainer, and tacking margins were cleaned and flattened. The perimeter of the reverse was cleaned mechanically with scalpels and then gum erasers, and vacuumed. A penetrating consolidant Plexisol P550 10% in white spirit was introduced into the reverse of the canvas in a 10 cm wide strip on the perimeter.





Fig. 7: Tear (Fig. 5), after alignment and flattening

The material chosen for strip-lining was 100% polyester Dacron<sup>®</sup>. It was prepared by fraying the inside edge. In the treatment of the first section, two coats of Plextol D360<sup>®</sup> thickened with Rohagit SD15<sup>®</sup> were applied to the strips of material. When dry, the material was heat-set to the reverse perimeter 10 cm in from the edge. After the bond proved too weak to withstand any stretching, a third application of adhesive was applied to the reverse of the original canvas. In the treatment of the second section, BEVA replaced the Plextol D360 because of its stronger bond.

#### Treatment of Tears

Before the painting was stretched on the Dutch Stretcher, the tears were reinforced. First, the old patches were removed by tearing them off in strips where possible. The adhesives and remnants of patch were then removed with a scalpel. There were some patches adhered with hide glue, but most were stuck on with polyester resin. Secondly, all tears were realigned by repeated local relaxation with low heat and moisture from slightly damp blotting paper. The edges of the tear were stretched and slowly brought closer together with the aid of tabs of masking tape. (Fig. 7) Thirdly, once any two edges of a tear touched, a bridging material was used. Only a small area of the tear was bridged at a time, allowing repeated relaxation and stretching of the canvas until the tear met all along its two edges.

For small tears and punctures, Lascaux Polyamide textile welding powder<sup>®</sup> was used. A thin line of powder was run along the edge of the tear on the reverse, then heated quickly through Mylar<sup>®</sup> with a heated spatula. The powder melts instantaneously at 82° C. At such a high temperature, care must be taken not to prolong contact with the heated spatula and canvas.<sup>5</sup> Pressure was applied locally until the polyamide set.

Larger tears were bridged with Devcon 5 minute Epoxy Resin<sup>®</sup>. Masking tape was used on the reverse to mask both sides of the tear just inside the edge. A bead of epoxy was run like a thread between the two strips of masking tape and worked in with a spatula. The area was covered with Mylar and left under pressure until cured. The excess was absorbed by the facing on the front and made removal of the excess quite easy.

Inserts were used when the original canvas had been lost, or where the original could not be completely realigned. The insert material was a combination of the original canvas, cut from the tacking margin, and polyester Dacron. This was bridged in the same manner as were the tears.

When the treatment of the tears was complete, silicon paper was used to cover the immediate area of the tear while temporary Reemay strips were adhered with BEVA. These strips supported the painting during stretching before the permanent patches were applied.

Now the painting was ready for the Dutch Stretcher.

#### Pre-Stretching

Restraint was provided by a Dutch Stretcher during the moisture treatment of the distortion of the canvas.<sup>6</sup>

This work strainer was constructed with lengths of 5 cm x 10 cm wood with one central vertical cross brace. The inside measurements of the work strainer were 4 cm larger than the painted surface of the canvas.

First, the painting was stretched on the work strainer face down on a table so that the entire reverse could be cleaned. The strip lining material was stapled to the strainer.

The canvas reverse was scraped with scalpels, debris was picked up with a vacuum, and soft gum erasers removed the embedded grime.

Pulleys were suspended from the ceiling, and ropes through the pulleys were attached to rings on the working strainer. This enabled the conservators to hoist the painting into the air, hold it vertically, and turn it over with ease. (Fig. 8)



Fig. 8: Hoisting painting on work stretcher

Once cleaned on the reverse, the painting was turned over, released from the work strainer onto the table, and remounted so that it lay with the reverse flat on the table. The tears had the facing tissue and excess epoxy resin removed. BEVA-prepared strips of Reemay were heat-set to the face of each tear to give it support. The strips of Reemay were then removed from the reverse of each tear so as to expose the reverse of the canvas entirely during the moisture treatment.

### The Low-Pressure Suction Unit

After the relaxation of the canvas using moisture, and the subsequent removal of planar distortion in the canvas, the painting must be dried under pressure in order to maintain this flat plane. This is the function of the Low-Pressure Suction Unit. It provides overall negative pressure under the painting during drying. Thus, the atmospheric pressure exerted on the surface of the painting ensures that distortion in the canvas does not reappear.

The design of this particular unit was developed from a survey of various models used for the low-pressure treatment of paintings. Although they function differently, and are used for diverse treatments, they are linked by a common theme or concept.

Similar moisture treatments on a smaller scale were made at the Central Research Laboratory in Amsterdam, Holland when the author assisted Mr. V.R. Me with the Cold Table Research.<sup>7</sup>

Bent Hacke uses the concept of low pressure combined with low heat in his suction apparatus in Aarhus, Denmark.<sup>8</sup>

Larger canvases have been treated Puccio Speroni at the Nationalmuseet in Brede, Denmark. The area upon which a large painting could be treated was extended by means of an air channel made of a porous sheet. This air channel extended from the surface of the suction table and allowed the entire surface of the large-scale painting to be held under pressure at one time.<sup>9</sup>

A simple suction table for paper conservation was constructed by Robert Futernick using P.V.C. pipes as air extraction channels around a core of transparent plastic for the suction table surface.<sup>10</sup>

Gustave Berger discusses the use of the painting as the top membrane in a vacuum lining.<sup>11</sup> A low-pressure air extraction unit he developed was demonstrated by Berger at the Painting Specialty Group of the American Institute of Conservation in Baltimore in 1983.

Some principles of all these systems were incorporated somewhat in the final design of the suction unit constructed for this project.

### Construction of The Low-Pressure Suction Unit

The wooden work table measured slightly larger than the work strainer. This was the base for the suction table. On all sides, a deep wooden outside edge supported the air extraction channel. This channel was made up of A.B.S. perforated soil drainage pipe<sup>†</sup> attached to the table with metal strapping. At the corners of the table, 90° elbow fittings were used. (Fig. 9) "T" fittings in the centre on each side of the table acted as ports for air extraction. These fittings held the channel together. The pipe was adjusted so that one row of perforations was located at the top, flush with the table surface. All other holes were sealed with tape. The pipes were sealed where they met the table with weather stripping and caulking.

Air was extracted from this air channel by attaching an industrial vacuum cleaner to each of the four ports on the piping around the table. For the suction to work across the surface of the table, sheets of open-pore polyurethane foam<sup>‡</sup> were butted together on the table, with edges extended to the extraction holes on the top edge of the pipes all around the table.

When a membrane, such as the painting or plastic sheeting, covered the surface of the foam and the vacuums were switched on, the system was self-sealing. Once the air was extracted from the foam, the atmospheric pressure working on the surface applied an even pressure overall.

### Moisture Treatment of Distortion

The ambient room temperature during the treatment was between 25° C - 30° C.

Sheets of washed muslin were laid on the polyurethane foam on the table and sprayed with water until moist. The painting, restrained on the work strainer, was placed on the table with its reverse in contact with the damp muslin. It was left under a plastic tent for about one hour. The muslin was removed, and the vacuums were switched on. Only the edges of the table were covered with a plastic film, up to the tacking margin of the painting, to seal off the air flow. The front of the painting was not covered. Low pressure was created under the painting, and the painting dried under pressure for five to six hours. This treatment was sufficient to remove the distortions caused by realignment of tears and the draping due to hanging with poor support on the original strainer.



Fig. 9: Suction table, detail of corner pipe





Fig. 10: Patched tear, (Fig. 4), detail, reverse, after treatment

### Consolidation

When the painting was completely dry, the reverse of the canvas was impregnated with Plexisol P550 and let dry overnight. The front of the painting was then consolidated by brushing on the Plexisol P550 while the painting was under pressure on the suction table, and left to dry.

### Reinforcing of Tears

Reemay was adhered with BEVA to the reverse of the tears. (Fig. 10) The temporary strips on the front were then removed.

### Panel Strainers

The original strainers gave inadequate support for the paintings so new panel strainers were prepared onto which the two sections were stretched. A wooden frame, constructed according to Sandra Lawrence's design from the previous year, was made up of lengths of wood measuring 5 cm x 10 cm with four vertical cross braces. The corners were butt joints reinforced with triangular plates made of aluminum for the first painting, and plywood for the second. The cross braces were also reinforced. The Gatorboard panel fit into a 1.25 cm rabbet strip on all perimeters and down the centre of each cross brace. The five panels were glued and screwed into the recess, resulting in a flat panel. Tyvar was stretched over the face as an interleaf. The painting was then mounted to the edges by means of the strip lining. Black plastic strips<sup>V</sup> were stapled on the edges to protect the tacking margin in transport and handling.

### Reintegration

Lacunae were filled with two materials. The deeper lacunae were filled with Mowiol 04M1<sup>W</sup>/calcium carbonate putty, building up layers gradually. Shallow holes were filled with Liquitex acrylic gesso.<sup>X</sup> A top coat of Liquitex was applied to all fills.

Inpainting was carried out using gouache paint.<sup>Y</sup>

### Varnish

Acryloid B72 12% in Cyclosol was used in a single spray application.

### Conclusion

By the measures taken in this treatment, it was possible to preserve these large, badly damaged paintings without lining.

The most interesting and useful result of this case study was the construction of a large-scale low-pressure suction unit with local, commercially available components. This allowed pressure to be applied to the surface of a large-scale painting evenly and with control. Although heat was not used in this case, the design could be adapted to incorporate it. If more air flow was desirable, a perforated table top could draw air down and away from the central area of the painting.

The low-pressure suction unit described in this paper is not widely used. The author hopes its application will continue to be developed and discussed.

### Acknowledgements

This paper was made possible by the practical work of Sandy Easterbrook, James Engelbert, Anita Henry, and Shelagh Young, conservators. Particular thanks goes to Nancy Hurn, Archivist, Canadian National Exhibition, for her involvement with the project. Thanks to Sandra Lawrence for her initial input into the project and her continuing interest. Thanks to Bob Arnold, Canadian Conservation Institute, for information on the previous treatments, to Charles Casement, editor and Valerie Clapperton, typist.

MaterialSupplier

- |  |  |
|--|--|
| a. <u>Plexisol P550</u><br>(Polybutyl methacrylate)<br>in USA known as: Rohamere P550  | Rohm, West Germany<br>North American Supplier: Monomer-<br>Polymer and Dajac Labs Inc.,<br>Trevose PA. USA                                 |
| b. <u>Plextol B500</u><br>(Methyl methacrylate copolymer<br>emulsion) in USA known as:<br>Rohamere B500                          | Rohm, West Germany<br>(see a)  |
| c. <u>Stabiltex</u><br>#4 plain weave (Polyester<br>crepe line)  | Swiss Silk Bolting Cloth Mfg. Co.<br>Zurich, Switzerland<br>Canadian supplier: B. & S.H.<br>Thomson & Co., Scarborough,<br>Ontario, Canada |
| d. <u>BEVA 371</u> adhesive  | Conservators Products Co.,<br>Chatham N.J. USA   |
| e. <u>Gatorfoam Board</u><br>1.25 cm thick rigid foam<br>laminated between plastic<br>surfaces                                   | Dow, Canadian Suppliers<br>E.M. Plastic and Electric<br>Products, Downsview, Ontario,<br>Canada  |
| f. <u>Pecap</u><br>Polyester monofilament<br>screen printing fabric  | Swiss Silk Bolting Cloth<br>Manufacturing Co.,<br>(see c.)   |
| g. <u>Typar</u><br>Polypropylene non-woven<br>fabric used in erosion control   |  |
| h. <u>Reemay</u><br>Polyester non-woven fabric   | Dupont Canada,<br>Supplier: Mackay Specialties<br>Canada Ltd., Toronto, Ontario,<br>Canada   |
| i. <u>Rhoplex AC634</u><br>Acrylic copolymer, probably<br>ethylacrylate/methyl<br>European name: Primal AC634                    | Rohm and Haas<br>Canadian Supplier: Rohm and Haas<br>West Hill, Ontario, Canada  |
| j. <u>Acryloid B72</u><br>Isobutyl methacrylate<br>polymer resin<br>European name: Paraloid B72                                  | Rohm and Haas<br>(see i.)  |
| k. <u>Cyclosol</u><br>High flash solvent   | Anachemia Chemicals Ltd.,<br>Mississauga, Ontario, Canada  |
| l. <u>Vulpex</u><br>Potassium Methyl<br>Cyclohexyl Oleate  | North American Supplier: Talas,<br>New York, NY, USA   |
| m. <u>Eltoline</u><br>Calendered tissue of<br>manilla and jute fibres  | Barcham Green and Co., Ltd.<br>Maidstone, England; Canadian<br>Distributor: Loomis & Toles Co.,<br>Ltd., Toronto, Ontario, Canada          |
| n. <u>Dacron 578-60</u><br>polyester multifilament<br>woven fabric   | Lincoln Fabrics Ltd.,<br>St. Catharines, Ontario<br>Canada   |
| o. <u>Plextol D360</u><br>Water soluble acrylic<br>resin dispersion based on<br>butyl acrylate<br>in USA known as: Rohamere D360 | Rohm, West Germany<br>(see a.)   |
| p. <u>Rohagit SD15</u><br>Polymethacrylate acid<br>thickener for Plextol D360<br>in USA known as: Rohamere SD15                  | Rohm, West Germany<br>(see a.)   |
| q. <u>Lascaux Textile Welding Powder</u><br>Polyamide  | Lascaux Restauro, Bruttisellen<br>Switzerland<br>USA Supplier: Fine Art Stretchers<br>& Services Inc., Brooklyn, NY, US                    |



<u>Material</u>	<u>Supplier</u>
r. <u>Mylar S-50</u> .005 mil polyester film	Dupont Canada Supplier: Cadillac Plastics Rexdale, Ontario, Canada
s. <u>Devcon 5 Minute Epoxy</u> Resin	Local hardware store
t. <u>ABS pipe 5 cm diameter</u> Perforated soil drainage pipe	Gravenhurst Pipe Co., Gravenhurst, Ontario, Canada Supplier: local hardware store
u. <u>Open-pore polyurethane foam</u> 30 pores per inch <sup>2</sup> used as wick in humidifiers	Engineered Foam Products Canada Ltd., Weston, Ontario Canada
v. <u>Black Plastic Strips</u> Franplas Art Conservation Edging Style 2823	Franklin Fiber-Lamitex Wilmington, Delaware, USA
w. <u>Mowiol 04M1</u> Internally plasticised polyvinyl Alcohol/polyvinyl acetate	Hoechst; Frankfurt, West Germany Canadian Distributor: Hoechst, Willowdale, Ontario Canada
x. <u>Liquitex</u> Acrylic gesso	Binney and Smith Inc., Easton, PA., USA Supplier: Artist Supply Store
y. <u>Gouache Paint</u> Omnigouache	J.M. Paillard, Mouy, France Supplier: Artist Supply Store

#### References

1. MacDonald, Colin S., A Dictionary of Canadian Artists, Volume 2, Ottawa, Canadian Paperbacks Publishing Ltd., pg. 343.
2. Robson, Albert H., Canadian Landscape Painters, Toronto, Ryerson Press, pg. 128.
3. Lawrence, Sandra, Report on condition of the Haines murals, 1985.
4. Bjarnhof, Mette, personal correspondence on the preparation of the Plextol D360, The Royal Museum of Fine Arts, Copenhagen, Denmark, May 1983.
5. Wakelin, Sally and Yates, Nicola, personal correspondence on the treatment of tears with Polyamide powder and Epoxy, National Maritime Museum, Greenwich, England, 1982.
6. Percival - Prescott W., Chittenden R., Lewis G. "Prestretched Low Pressure Lining Methods." Conference on Comparative Lining Techniques, National Maritime Museum, Greenwich, England. April 1974.  
  
Mehra, V.R. "Cold-lining and care of the paint layer in a triple-stretcher system", ICOM Committee for Conservation, 78/2/5, Zagreb, 1978.  
  
Hacke, Bent, "A low-pressure apparatus for treatment of paintings". ICOM Committee for Conservation, 78/2/12, Zagreb, 1978.
7. Mehra, V.R., "Further developments in cold-lining (nap-bond system)", ICOM Committee for Conservation, Venice, 1975.
8. Hacke, Bent, "Low pressure - Heat, moisture, stretching. Notes on further developments," ICOM Committee for Conservation, Ottawa 1981.
9. Speroni, Puccio, presentation for the working group Meeting Structural Restoration of Canvas Paintings, ICOM Committee for Conservation, Ottawa 1981.
10. Futernick, Robert, "Leaf casting on the Suction Table" AIC Book and Paper Group 10th Annual meeting Milwaukee 1982.
11. Berger, G., "Vacuum lining without a membrane", AIC paintings Group, 11th annual meeting Baltimore 1983.





## SUMMARY

This paper attempts to give a guide as to the likely bond strengths achieved when these adhesives are applied at particular thicknesses and bonded at particular temperatures on a Willard hot table. In all hot table experiments a fine weight pre-primed linen canvas is bonded to polyester sailcloth under a pressure of 38cm. H<sub>2</sub>O. Some sizing of the lining fabric was done using B72, and some initial tests with solvent activation were carried out.

Beva 371 gel was capable of forming very strong bonds, but a thickness or coat weight of 10g/m<sup>2</sup> dry adhesive bonded at 50°C gave a good strength of 100g/2.5cm. on the Courtauld hot table.

Beva 371 gel on sized cloth gave similarly strong bonds, but these bonds were more prone to adhesive transfer.

Beva 371 film gave extremely high bonds of over 5,000g/2.5cm. if used in multiple layers. One layer needed a temperature of at least 62°C to form a bond of around 700g/2.5cm. - again on the Courtauld hot table.

Plextol D360 gave very adequate initial bonds, and the bonding temperature and thickness could be balanced against each other to obtain a required initial strength. With a coat weight of 70g/m<sup>2</sup> at a bonding temperature of 35°C, 550g/2.5cm. was achievable, when tensile tested at four weeks. A lighter coat of 100g/m<sup>2</sup> bonded at 55°C gave a similar bond strength result.

Both Beva 371 and Plextol D360 could be successfully solvent activated by brushing on the solvent; some heat was required with Beva.

## THE BOND STRENGTHS OF TWO HOT TABLE LINING ADHESIVES - BEVA 371 AND PLEXTOL D360

Juliet J. Hawker  
Courtauld Institute of Art  
London, England

Introduction

Beva 371 and Plextol D360 are both modern thermoplastic, copolymer, lining adhesives. The lining survey in 1984<sup>1</sup> has shown Beva 371 to be particularly popular, yet there is little quantitative information of possible bond strengths available, and when bond strengths have been quoted the film thickness has rarely been mentioned, despite it being critical to the strength.

Today there is a strong move towards minimalist treatments and concern about adding to the stresses within the structure of the painting. Not only do we need to know whether a bond is too strong or too weak, but Mehra has perhaps made us more aware that each painting lined might require a different strength of support depending on its structural composition, condition, size and weight. It is therefore important to know more about the adhesives to enable their effective use in a minimalist manner.

Unfortunately the tests described below are limited, for quantitative investigations in the field of conservation tend to be rather specific to the particular practices and materials used at the particular testing institute, in this case, those used currently at the Courtauld. On the other hand we are gradually piecing together some basic rules and patterns to do with adhesive strengths.

Experimental: - General Test Procedure.

The Hot Table. The table at the Courtauld Institute is an early model. It had to be tested to find an area of most even heating on which the tests were carried out. This was done using a thermo couple and testing the temperature of the bed at 15 evenly spaced points, while increasing the temperature in 5°C steps. Also the difference between the temperature sensors on the bed, and that on the dial of the control box was recorded, so that accurate temperatures could be calculated for the tests. The experiments were thus reproducible and accurate to within  $\pm 1^\circ\text{C}$ .

A vacuum was made by employing two sheets of Melinex, sealed with White spirit, plus a string breather and paper towelling strips for air transfer around the samples. Two cardboard pads supported the suction tubes. The area within the string diaphragm was spot checked for evenness of vacuum.

So that the pressure could be measured accurately a water column was used with a tube running directly off the bed of the table. 38cm. H<sub>2</sub>O was used for all tests on the hot table, this being just over 1" Hg follows the general trend to use lower pressures.<sup>2</sup>

Table Procedure. The samples were placed in a row between the sheets of Melinex, and the air was then evacuated. At lower temperatures it took 15 - 20 minutes for the bed to reach the desired temperature, at higher settings it took 25 - 35 minutes. As soon as the activation temperature was reached the table was switched off. The bed tended to stay at the set temperature for 3 minutes before any cooling could be detected. The table has no cooling fans and the samples were left on the bed for 1½ hours under vacuum pressure, while the table cooled slowly. This time remained constant even though the cooling time was less for the lower temperatures.

Fabrics. To simulate a painting primed canvas was used. A finely woven Belgian linen, 305g/m<sup>2</sup> and 0.034mm. thick, was bonded to Polyester sailcloth, 174g/m<sup>2</sup> and 0.025mm. thick. These two fabrics were used for every test; ideally more than one type of lining fabric would have been tested but time did not permit this. Sailcloth was chosen because of its relative imperviousness to the adhesives, and because it is currently used regularly at the Courtauld Institute.<sup>3</sup> A fine weave linen was chosen as a mock painting as it was thought a finely woven fabric would be a more exacting test for the tensile strength of a bond.<sup>4</sup>

Peel Tests. Peel tests are currently thought to provide more relevant information on the bond strengths of linings than lap shear tests. Peel tests may not be ideal, but they yield a wider range of information. They are more sensitive and record the uniformity of a bond and type of wetting, as well as monitoring the resistance to out of balance shear forces.<sup>5</sup> D. Findlater<sup>6</sup> suggests that results from lap shear tests can be misleading as the strength depends to a large extent on the mechanical properties of the adherends, which can distort excessively, also there is an element of peel in all lap shear tests.

The tests were carried out at one week and four weeks after bonding, with some Plextol D360 samples tested after four months and one year. Thus other than those of Plextol D360, only two samples from each experiment were tested. Particularly because of this, it must be emphasized that, at best, the values given can only be taken as an indication as to the sort of bonds achievable, following the same method and using the same fabrics. For more statistically accurate results further samples need to be tested. It is also important to remember that

results will be affected by the particular behaviour of each hot table.

Testing was carried out on the Instron tensile tester, model 1026, and ASTM D903-49, modified - with a speed of 2mm/min. was the test procedure used.

Values are given in grammes (per 2.5cm. - the width of the sample), this is the mass embodied in the force resisting crosshead movement.<sup>7</sup>

The room temperature where the peel tests took place was kept between 18 - 23°C during testing, with an RH. of 45 - 55%. Occasionally the RH. dropped below this, but the changes in conditions did not appear to effect the peel strength of the samples.

All the 'one week' samples (100), were peeled for 7.5cm., while the 'four week' samples (100), were peeled for at least 2.5cm., and then a further 4-8cm. at a high speed of 100mm/min. to check on the evenness of the strength of the sample. The 'four months and one year' Plextol D360 samples were peeled in the same way as the first batch. Results are recorded for the low speed only.

#### Preparation of samples

Beva 371 Gel Samples. The same tin of Beva 371 was used for all the linings, was manufactured by Lascaux in Switzerland. For each coat of Beva a specific amount of adhesive was mixed with Petroleum spirit to dilute the Beva by 20%. The mix was warmed until clear and then rolled on to the sailcloth using a sponge roller, regularly moving the roller back and forth and across in even strips, to apply an even coat.

250g/m<sup>2</sup> of adhesive in solvent was applied for each of 3 coats. 6 hours drying time was left between each coat, and 24 hours were left before bonding.

To find out how long it took for the solvent to evaporate from the solvent film one sample was weighed straight after applying one coat, and at intervals after that. After 24 hours of room temperature evaporation virtually ceased.

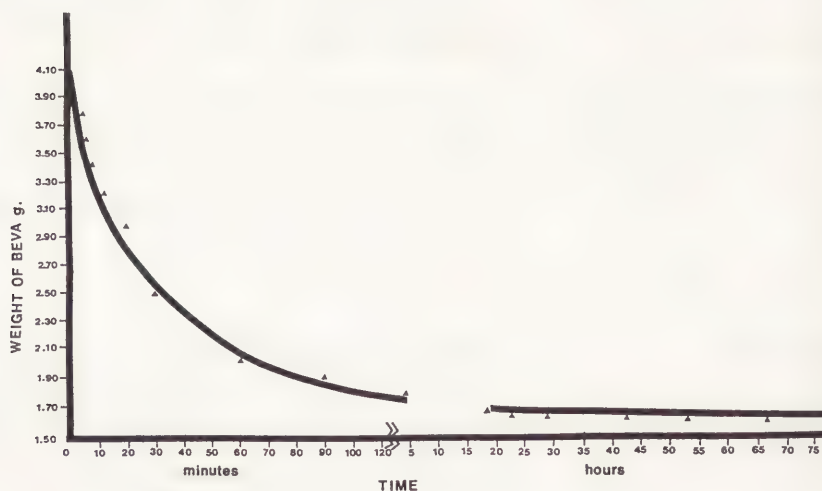


Fig. 1. Evaporation of Solvent from Beva 371

The samples were all weighed and measured so that the coat weight and thickness of the adhesive was calculated.

Coat No.	Mean Weight g/m <sup>2</sup>	Mean Thickness mm
1 Beva 371 gel	80	0.045
2 Beva 371 gel	160	0.13
3 Beva 371 gel	240	0.215

The first coat impregnates the sailcloth so that it is approximately half the thickness of the following coats, which are about 0.08mm. thick. (Approximately the same thickness as the Beva film).

The bonding temperatures used with the Beva gel samples were from 50°C to 75°C going up in 5°C steps.

Beva 371 Gel Samples on Sized Sailcloth. Paraloid B72 was used to size the cloth. 200g/m<sup>2</sup> of B72 plus solvent, (20% resin in dimethylbenzene), was brushed on. Once the sizing coat was dry the Beva gel coats were applied as above.



Coat no.	Mean Weight g/m <sup>2</sup>	Mean Thickness mm
1 Beva 371 + B72	100	0.075
2 Beva 371 + B72	180	0.145
3 Beva 371 + B72	260	0.23

The B72 sizing adds 20g/m<sup>2</sup> to the first coat. Consecutive coats of Beva 371 gel weigh 80g/m<sup>2</sup>, the same as the Beva gel samples on unsized fabric. The sizing prevents the first Beva coat from impregnating the sailcloth, and therefore the first coat is about the same thickness as the second and third coats on sized and unsized fabric.

The bonding temperatures used with these sized sailcloth samples were from 50°C to 70°C going up in 5°C steps.

Beva 371 Film Samples. Pieces of Beva film were simply cut out and placed on to the sailcloth in one, two and three layers. The film was found to be 70g/m<sup>2</sup> in weight, which is 10g less than one rolled coat of Beva gel, but the thickness is about the same as one non-impregnating coat of the Beva gel.

The bonding temperatures used with the Beva film samples were from 50°C to 80°C going up in 5°C steps.

Plextol D360 Samples. All the Plextol D360 came from the same 5 litre container, and was mixed with the thickener Rohagit SD15, two different recipes were tried. The first using 1% w/w thickener only, the other using 2.5% w/w thickener with 0.5% of 25% strength NH<sub>4</sub> in 1:10 H<sub>2</sub>O added. The recipes produced little variation in bonding strength. In any case the amount of thickener of NH<sub>4</sub> depends on how old the adhesive batch is, and how much adhesive is required, - NH<sub>4</sub> will have evaporated from old adhesive, while a more porous lining fabric will need a more thickly applied layer.

Two methods of applying the adhesive were used, screening through a wide mesh made of stretched net curtain fabric, and rolling using a sponge paint roller and tray. One screened coat was roughly equivalent to two rolled coats in coat weight and thickness, both left a textured surface.

Approximately 400ml/m<sup>2</sup> of adhesive was screened for each coat, and up to 4 coats were applied.

Coat no.	Mean Weight g/m <sup>2</sup>	Mean Thickness mm
1 screened D360	100	0.09
2 screened D360	190	0.17
3 screened D360	280	0.25
4 screened D360	370	0.33

The first coat screened on to the smooth surface of the sailcloth deposits about 10g more adhesive than the following coats over the textured adhesive surface.

Some samples were prepared on sized fabric, in the same way as the Beva gel samples, but because the Plextol was mixed so that it did not impregnate the lining fabric the % increase in thickness due to the sizing was small, and thus the sized samples showed only a slight increase in strength.

The bonding temperatures used with these Plextol samples were from 30°C to 55°C going up in 5°C steps.

#### Solvent Activation of Samples.

At low temperatures the possibilities of solvent activation were briefly investigated with some samples of Beva gel on sized sailcloth, Beva film and Plextol D360. The adhesives were applied as above to the lining fabric, allowed to dry, and then brushed with solvent. 100ml/m<sup>2</sup> of a mixture of an aromatic and an aliphatic hydrocarbon, or sometimes just an aliphatic hydrocarbon, was used. When solvent activating Beva film the instructions supplied with the film should be noted and the edges of the film should first be tacked down to the lining fabric with a heated spatula, else the film will crinkle and roll up. After brushing, the samples were covered straight away with the simulated painting canvas and either dried on the hot table or on an air flow table without heat. When the air flow table was used the pressure was set at 25cm H<sub>2</sub>O with 10m/sec. air flow for 10 mins., then at 15cm H<sub>2</sub>O with the air flow at 20m/sec. for 90 mins.

### Results.

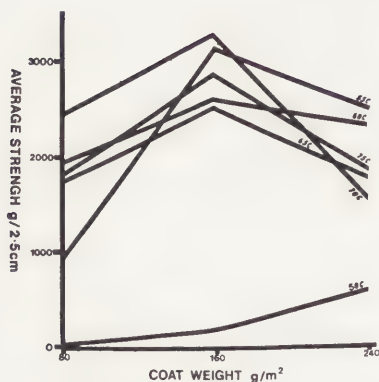
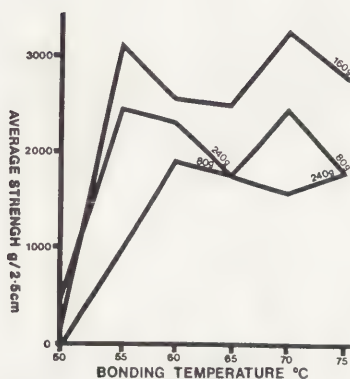


Fig. 2



Figs. 2 and 3. The peel strengths of Beva 371 gel when bonded on the hot table with different bonding temperatures and coat weights

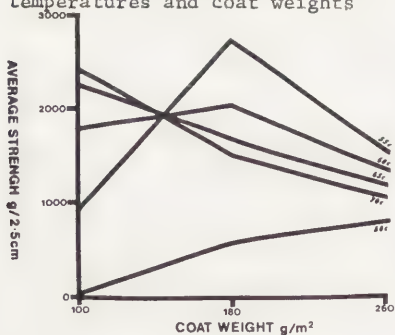
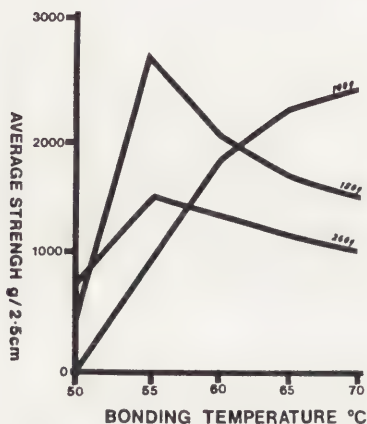


Fig. 4



Figs. 4 and 5. The peel strengths of Beva 371 gel on sized sailcloth, with different bonding temperatures and coat weights, bonded on the hot table.

Both graphs show that Beva gel is capable of producing very strong bonds, and that a coat weight of  $160\text{g/m}^2$  is stronger than  $80\text{g/m}^2$  or  $240\text{g/m}^2$  above  $50^\circ\text{C}$ . Most of these results are actually too strong if the Phenix - Hedley parameter<sup>8</sup> is used as a guide. This is that  $300\text{g}/2.5\text{cm}$  is about the lowest limit for a lining strength, with  $800 - 1,000\text{g}/2.5\text{cm}$  forming a good - to - strong bond. In this instance a coat weight of  $160\text{g/m}^2$  bonded at  $55^\circ\text{C}$  is three times larger.

A coat thickness of around  $80\text{g/m}^2$  bonded at  $55^\circ\text{C}$ , or perhaps a coat of  $240\text{g/m}^2$  bonded at  $50^\circ\text{C}$ , - if the weight of the adhesive is not so important, will possibly give adequate bonding.

Fig. 3 indicates that the strengths first peak at  $55 - 60^\circ\text{C}$ , and there appears to be relatively little or no increase in strengths with higher temperatures.

$55^\circ\text{C}$  is a fairly low bonding temperature for Beva, but it should be remembered that the hot table used, often took 25-35 mins. to reach the desired temperature, and a longer time to cool, so that 15-20 mins. was spent close to the activation temperature. This gives plenty of time for the lower molecular weight adhesive components to flow and for wetting to occur, i.e. the longer the table takes to heat and cool the lower the activation temperature needs to be, within a certain range. With a more efficient table with cooling fans, a higher temperature will be needed because of the shorter time the adhesive is subjected to the heat.

The graphs in figs. 4 and 5 show broadly similar results to those on unsized lining fabric, but with lower temperatures a thicker coat is strongest, a middle weight coat is strongest with intermediate temperatures, and a thinner coat strongest with higher temperatures. The size layer causes delamination to occur more readily and so most results are weaker. The relationship between the coat weight, the bonding temperature used, and at what interface the delamination took place is complex, but for the two strongest results -  $100\text{g/m}^2$  bonded at  $70^\circ\text{C}$ , and  $180\text{g/m}^2$  bonded at  $55^\circ\text{C}$ , the delamination was caused by cohesive failure of the adhesive rather than delamination at an interface.

The graphs in figs. 6 and 7 show the very high bond strengths obtainable with two and three layers of Beva film; mostly, unlike Beva gel, the strength increases with adhesive thickness. When Beva film is bonded at  $55-60^\circ\text{C}$  it is too weak (shown most clearly in fig.7), a temperature of at least  $62^\circ\text{C}$  is needed for a good bond on the Courtauld hot table. Accurate measuring of the temperature was found to be important because at  $65^\circ\text{C}$  the bond strength was already rather high.

Generally the strengths shown by Plextol after four weeks are less than Beva, and there is a fairly uniform increase in strength with an increase in coat weight and bonding temperature. This means that in practice the initial strengths are more controllable, and as long as the bonding temperature is not too low the accuracy of the temperature is not so crucial. However, to get high initial bond strengths at low bonding temperatures a thickish coat weight was required.

After four months the bond strengths had mostly increased, at one year the increase had stopped. The amount of increase was generally greater for the samples with lower coat weights bonded at lower temperatures, suggesting that the higher values had reached a strength limit at about four months or before. Increases in strengths with time may possibly be due to the continued cold flowing of the adhesive so that it conformed more closely to the fabric, but there is likely to be other factors involved, and particularly at  $30^\circ\text{C}$  anomalies occurred. More testing is therefore needed to verify the change in the bonding patterns with ageing. Although the strength increases are not generally big enough to be liable to cause reversability problems.

### Solvent Activation of Beva Gel on Sized Sailcloth

Solvent	Bonding Temp. $^\circ\text{C}$	Coat No. + Ct. Wt. $\text{g/m}^2$	Peel strengths in g.		
			Ave.	Min.	Max.
80% cy + 20% mb	55	2 - 180	2,700	1,825	3,900
100% mb	50	2 - 180	2,750	1,800	3,800
80%cy + 20%mb	40	2 - 180	1,450	1,550	2,100
80% cy + 20%mb	35	2 - 180	1,100	800	1,400

cy = cyclohexane  
mb = methylbenzene



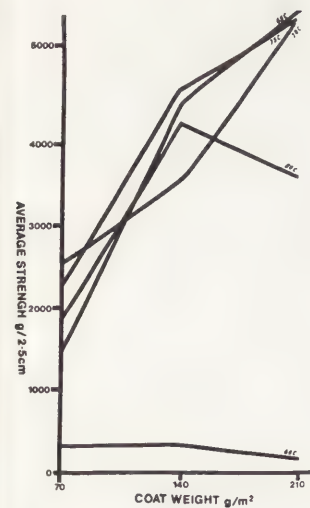
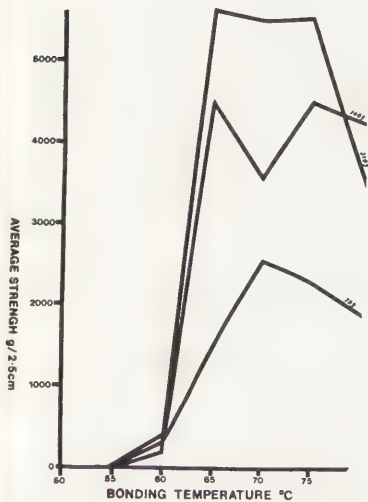


Fig. 6



Figs. 6 and 7. The peel strengths of Beva 371 film when bonded on the hot table with different bonding temperatures and coat weights of the adhesive.

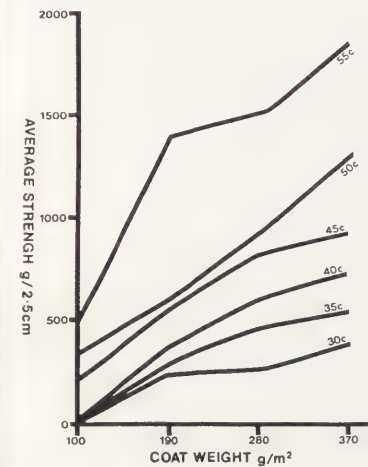


Fig. 8

The results above are only for the coat weight of 180g/m<sup>2</sup>; later tests have shown that a coat weight of 100g/m<sup>2</sup> is adequate as it gave similarly strong bonds at 35°, and if Petroleum spirit was used instead of Cyclohexane bonds tended to be a bit stronger. Further tests could be carried out using a lower coat weight still and different activating solvents, although it seems that 35°C may be about the lowest temperature usable, and that some aromatic content is needed in the solvent. It must be noted that these samples were brushed with solvent, as spraying Beva with solvent has, so far, been far less successful, it appears the dry adhesive needs to be disturbed to allow the solvent to mix with it. When sprayed, the particular solvents used tended to run off or run into pools resulting in either very weak or very strong bonds.

It was noticed that straight after bonding, the solvent activated Beva gel bonds sealed at 50°C and below, were weak. They had to be left for a day for the strength to build up. It seems that total evaporation is necessary for a good bond, and an early test on an 80g/m<sup>2</sup> Beva sample showed that 24 hours were needed at room temperature (fig.1).

Solvent activation of Beva Film

Solvent	Bonding Temp. °C	Coat No. + Ct. Wt. g/m <sup>2</sup>	Peel strengths in g.		
			Ave.	Min.	Max.
100% mb	55	1 - 70	1,200	500	2,300
100% mb	55	2 - 140	2,400	1,850	2,900
80% cy + 20% mb	55	1 - 70	850	550	1,300
80% cy + 20% mb	55	2 - 140	1,925	800	3,550*
80% cy + 20% mb	45	1 - 70	800	350	950
80% cy + 20% mb	40	1 - 70	240	80	460
cy = cyclohexane mb = methylbenzene			*High peak probably due to an uneven application of brushed solvent.		

This table indicates that a temperature of 45°C is needed for a good bond using 100g/m<sup>2</sup> of brushed solvent on one layer of Beva film. There is likely to be more solvent in a coat of Beva gel which may account for the fact that, under these test conditions, the gel bonded at low temperatures gave stronger results than the film. Again these results are rather specific to our hot table.

Solvent Activation of Rolled Plextol D360

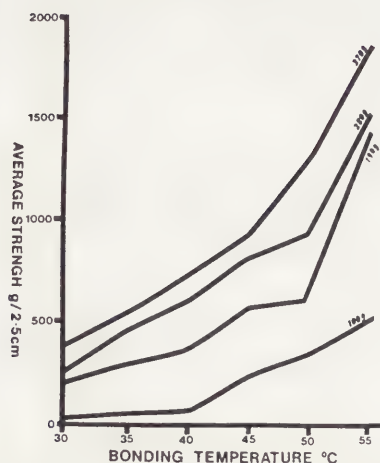
(Results are a mean of one week and four week tests samples)

Solvent	Bonding Temp. °C	Coat No. + Ct. Wt. g/m <sup>2</sup>	Peel strengths in g.		
			Ave.	Min.	Max.
65% cy + 35% mb	40	4 - 222	2,300	1,800	2,550
65% cy + 35% mb	35	4 - 222	1,725	1,500	2,050
65% cy + 35% mb	12*	4 - 222	2,450	2,000	3,400
100% mb	14*	4 - 222	1,150	540	2,060 **
cy = cyclohexane mb = methylbenzene			* Room temperature while samples were bonded on the air flow table **This last result is the mean of two samples both peeled after one week		

The strengths are all high and the last two results suggest that no heat is required when solvent activating Plextol D360. In fact the table shows that the unheated sample brushed with 100ml/m<sup>2</sup> of 65:35 cyclohexane to methylbenzene is stronger than the sample heated to 40°C. There is no explanation for this as yet, but it may possibly be related to the time the solvent takes to evaporate. Again, more tests are required for a pattern of results to emerge. All the samples increased in strength after four months, and those bonded with heat increased more than the samples dried on the air flow table.

All the solvent activation tests described here were preliminary; spraying D360 with solvent does work but more solvent per m<sup>2</sup> is often necessary as when spraying more solvent is wasted. Also with a larger surface area to cover more solvent will evaporate before the painting is positioned on top and the drying started. A drop lining is likely to require extra solvent too as the already heated table will cause faster evaporation.

More recent experiments with brushing and spraying of lower coat weights of D360 with 100ml/m<sup>2</sup> of Petroleum spirit, and drying the samples on an air flow table with no heat, gave higher bonds than Cyclohexane; however, strengths obtained with Cyclohexane are adequate. Again brushing gave higher strengths



Figs. 8 and 9. The peel strengths of Plextol D360, - peeled after 4 weeks, when bonded on the hot table with different bonding temperatures and coat weights of the adhesives.

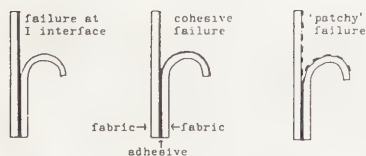


Fig. 10. Different types of failure.

than spraying when using equal amounts of solvent, but brushing may be less practical on a larger scale. Amounts of solvent needed when spraying will vary with the "style" of the person spraying, thus without the use of a robot it is difficult to quantify this very exactly. (For a less flexible lining, tests on the solvent activation of coat weights of 100g/m<sup>2</sup> of Plextol B500 and Plextol D498 have found these adhesives to give strong bonds when spray activated with approximately 300-400ml/m<sup>2</sup> of Methylbenzene, less toxic Propan 2 ol can be used also. The ageing of both these adhesives has so far been found to be good if they are thickened with Rohagit SD159)

Whether spraying or brushing solvent practice is needed to get as even a layer of solvent as possible, uneven solvent application will give uneven bonding.

#### Bond Failure and Adhesive Transfer.

When looking at the samples overall it seems that, as expected, a less nap bond gives a stronger bond, however, this was not actually always the case as sometimes it depended on the type of failure. At lower strengths, below 1,000g/2.5cm, the failure was always at the canvas to adhesive interface, with no adhesive transfer. At higher strengths there was a cohesive failure, or a failure at the adhesive to sailcloth interface. With thicker adhesive on unsized cloth a patchy type of failure occurred, with patches wholly left on the canvas or wholly left on the lining fabric.

Plextol D360 generally had weaker, more nap bonds, and was therefore less prone to adhesive transfer. Both screening and rolling produced a textured surface of adhesive, resulting in less area of contact. If bonded at a heavy coat weight with a high bonding temperature, or solvent activated, some adhesive transfer may result, but because of the rubbery nature of Plextol D360 it can be picked off cleanly, it has a strong cohesive force. Being slightly tacky at room temperature the Plextol has more 'grip' on the smooth surface of the sailcloth than Beva.

The sized sailcloth caused the Beva samples to transfer more readily. The B72 made the fabric very smooth, and probably adhesive transfer would be less likely if a coarser lining fabric was chosen. Due to the problem of adhesive transfer there is no real advantage in sizing a relatively non-porous fabric like sailcloth, yet sizing may be useful on more porous material, as less adhesive would then be required.

This information on the types of failure is, again, only based on two or three samples for each test; these samples are unaged and peeled at 2mm/min. A bond will behave differently after ageing and when peeled at a different speed; however, it does appear that if a bond strength remains constant or increases in strength with time, it is better to limit the initial strength for safe and easy reversibility. A strong bond may require heating to high temperatures for reversal, or the use of solvents or scraping the back of the canvas for partial reversal.

#### General Conclusion

Good bonds can be achieved at significantly lower bonding temperatures than those often employed on the hot table, although the behaviour particular to individual tables will affect the bond strengths of a lining.

Beva gel appears to have an optimum thickness for strength, but this can produce bonds which may be too strong. Accurate measuring of the bonding temperature is particularly important when using Beva film because of the small difference in temperature that can produce weak or strong bonds.

If further tests prove Plextol D360 to be reasonably stable it will have some advantages when a minimal lining is required as:

- it is non-toxic
- it seems to have more controllable bond strengths when heat sealed
- it seems not to be prone to adhesive transfer
- low bonding temperatures can be used
- it is non-impregnating
- it is very flexible
- it can be solvent activated and dried without heat.

Although the bond strengths do increase during the first year and more strength tests are needed, the adhesive has been used in Denmark for the last eighteen years, and some linings that have been taken apart have not, apparently, caused problems to date. Other less flexible Plextols may also prove to be useful.

It must be stressed that the results given are only preliminary and can only be used as a rough guide when using the same conditions and materials, but from a wider view point they do illustrate that the coat weight of the adhesive has as much influence on the bond strengths as the bonding temperature.



### Acknowledgements

This article is based on a project carried out at the Courtauld Institute. Thanks to Gerry Hedley for advice and practical help, also to Alan Phenix for his initial testing of Plextols while at the Institute.

### Notes and References

1. G.A. Hedley and C. Villers, "Lining in 1984: Questionnaire replies", ICOM Committee of Conservation, 7th Triennial Meeting, Copenhagen (1984), vol.1, section 2, 84.2.26.
2. *ibid.*
3. G.A. Hedley and C. Villers, "Polyester sailcloth fabric: A high-stiffness lining support". Science and Technology in the Service of Conservation, IIC Washington Congress, pp. 154-158.  
also: -  
G.A. Hedley, "The stiffness of lining fabrics: Theoretical and practical considerations", ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa (1981) Preprint 81.2.8.
4. A. Phenix and G.A. Hedley, "Lining without heat or moisture", ICOM Committee for Conservation, 7th Triennial Meeting, Copenhagen (1984), vol.1, section 2, 84.2.38  
also: -  
A. Phenix, an unpublished paper given at the students' symposium at the Tate Gallery (1985).
5. *ibid.*
6. D. Findlater, "New clues to glues in action", New Scientist (21st Nov., 1985) pp41-49.
7. The SI measurement of  $\text{Kg/m}^2$  is not used in these tests because whole numbers are preferred, and the samples are only 2.5cm in width, therefore do not yield information as to the strength over 1m., however,  $0.5\text{Kg}/25 \times 10^{-3} = 500\text{g}/2.5\text{cm}$ .
8. A. Phenix and G.A. Hedley, "Lining without heat or moisture", ICOM Committee for Conservation, 7th Triennial Meeting, Copenhagen (1984), vol.1, section 2, 84.2.38.
9. E. de Witte, S. Florquin and M. Goessens -Landrie, "Influence of the modification of dispersions on film properties", Adhesives and Consolidants IIC Paris Congress (1984), pp. 32-35.  
also: -  
K. Ketnath, "The use of acrylic resins and the heat seal method for the conservation of paintings on canvas", Maltechnik - Restauro 4 (1983), pp. 257-268.

### Materials

Belgian linen canvas no.706, has one coat of Safflower oil priming. Plain weave, 23 weft per cm, 16 warp per cm. Directly imported by Green and Stone Ltd., Fine Art Suppliers, 259 King's Road, London SW3.

Polyester sailcloth, quality: 00169/1A, colour: Scour, Brand: 18L. Plain weave, heat pressed, 22 weft per cm, 24 warp per cm. Supplied by John Heathcoat & Co Ltd., Tiverton, Devon EX16 5LL.

Beva 371 gel (Lascaux Restauro). An adhesive based on an Ethylene vinyl acetate copolymer. Supplied in U.K. by Frank W. Joel Ltd., Oldmedow Rd., King's Lynn, Norfolk PE30 4HH.

Paraloid B72 (Rohm & Haas). An acrylic copolymer resin: Ethylmethacrylate methyl acrylate 70:30. Supplied by Rohm and Haas (U.K.) Ltd., Lenning Hse., 2 Masons Ave., Croyden CR9 3NB.

Beva Film. The Beva film used in these tests was manufactured by the Adam Chemical Co. USA. It was a  $3\frac{1}{2}$ mil. thick film, in a roll 27" wide, 20" long (68.6cm x 609.6cm.). Production problems have led to a new version made by another company. This is supplied in the U.K. by Frank W. Joel, address as above.

Plextol D360 (Rohm GmbH). An acrylic copolymer resin: n-Butyl methacrylate methyl acrylate. Supplied in U.K. by Cornelius Chemicals Ltd., St. James's Hse., 27-43 Eastern Road, Romford, Essex RM1 3NN.

Rohagit SD15 (Rohm GmbH). Used to thicken Plextol D360, it is a polymethacrylic acid. Suppliers in U.K. are Cornelius Chemicals Ltd, address as above.

Screen mesh. A net curtain fabric of plain weave with 1mm spaces between weft and warp threads. Available from John Lewis Dept. Store, Oxford St., London W1.

Petroleum spirit (B.D.H. Chemicals). An aliphatic hydrocarbon. Weight per ml. at 20°C approx. 0.75g, distillation - 120°C to 160°C. Suppliers are B.D.H. Chemicals, Poole, Dorset.



## SUMMARY

The evolution of the structure of paintings belonging to the end of the XVIIIth - beginning of the XIXth centuries is discussed and the analysis of characteristic damages of ground and paint layer of canvases, painted in different techniques, is presented in the report. Results of experiments on modelling typical damages by means of the method of accelerated heat and moisture ageing of samples imitating certain elements of the structure of painting are cited. Practical recommendations are proposed as to correcting traditional methods of restoring paintings belonging to this period with regard to technical and technological characteristics of a painting. A new method of stabilizing paintings without lining them on a new support is put forward.

THE CHOICE OF A METHOD OF TECHNICAL RESTORATION OF EASEL OIL PAINTINGS DEPENDING ON SPECIFIC TECHNICAL AND TECHNOLOGICAL FEATURES OF A PAINTING (ON THE EXAMPLE OF RESTORING WORKS BY RUSSIAN PAINTERS, BELONGING TO THE END OF THE XVIIIth - BEGINNING OF THE XIXth CENTURIES)

E.Yu.Ivanova, T.S.Fedoseeva  
All-Union Research Institute of Restoration (VNIIR)  
Krestyanskaya pl., 10  
Moscow 109172  
USSR

The investigation of painting technique and elaboration of methods of its restoration have been developing independently; at the same time specialists in practical restoration did their best to find universal methods independent of painting techniques and applicable to works of different painters that worked in different styles and different epochs. Experience has shown that there are no universal methods of the kind, and in every case the restorer has to correct methods of restoration; when choosing his techniques he must inevitably take into account the type and condition of the ground, the way of applying the paint layer and character of damages, relying only on his own intuition and experience.

This work does not claim to provide a final solution of the problem of interaction between technical and technological properties of painting and restoration methods, however, on the basis of analyzing a large number of works of painters worked at the end of the XVIIIth - beginning of the XIXth centuries, the authors tried to reveal the most characteristic types of damages that occurred due to specific techniques of painting typical of this time, and put forward some changes to be made in standard methods, accounting for the type of grounds and method of applying a paint layer.

It is very important to reveal the specific character of restoration problems and to work out an approach to their solution in conformity with paintings of the investigated period, since museums of our country contain a lot of works of this time.

Problems of evolution of the structure of paintings belonging to the end of the XVIIIth - beginning of the XIXth centuries are discussed in the report, and the interaction between the character of typical damage and technical types of painting is revealed. The results of modelling typical damage by means of accelerated heat and moisture ageing of samples, imitating separate elements of the structure of painting of that time, are given. The report contains practical recommendations as to correcting traditional methods of restoring paintings with regard to painting techniques, as well as the description of a new method of stabilizing without lining them on a new support.

1. The investigation of evolution of the structure of paintings belonging to the end of the XVIIIth - beginning of the XIXth centuries; the analysis of typical damage and description of traditional methods of restoration.

Specific features of painting techniques of the investigated period which become decisive when choosing restoration methods and are mainly connected with the composition and methods of preparing grounds and ways of applying a paint layer, this, in the long run, determining processes of ageing and the character of further decay of painting.

A systematical investigation making use of modern methods of analysis (X-ray and structural analysis, IR-spectroscopy, microchemical methods of analysis and so on), of 23 paintings, especially selected from different museums of the country and reflecting the most characteristic painting techniques of painters, who worked in Russia during that period, has been carried out in order to solve the problem.

Investigations have shown that the composition of paintings of this period had a clear tendency to changing from single-layer red-brown glue grounds at the beginning of the XVIIIth century to double-layer ground which appeared in the second half of the XVIIIth century and consisted of the lower coloured glue layer and the upper much more bright coloured layer, containing white lead paint. The amount of white lead paint in grounds increases, starting from the 90-s of the XVIIIth century, and it becomes the main filler at the beginning of the XIXth century, ousting



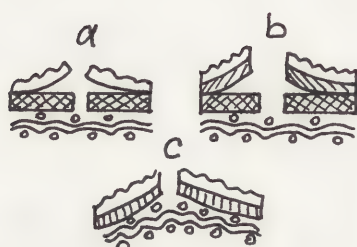


Fig. 1: Typical painting decay on different type grounds; a - glue ground; b - double-layer ground; c - oil ground.

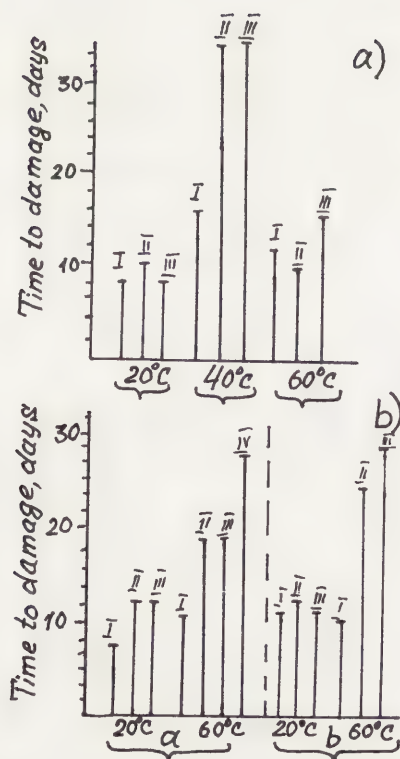


Fig. 2: Ageing diagrams for modelling ground (a) and colour layer samples (b); (a) I - glue ground, II - oil ground, III - double-layer ground with oil imprimatur; (b) I - ground, II - red ochre paint layer; III - white lead paint layer; IV - with mastics lacquer. (a - glue ground, b - oil ground).

ochre completely; oil grounds appear, and by the end of the XIXth century they gradually oust glue and double-layer grounds with oil imprimatur.

Microchemical analysis of grounds of paintings under experiment showed that ochre, chalk, and later - white lead paint were the most typical fillers of that period. At first, animal glue was used as a binder; however, in grounds one can always detect average amounts of oil which is either an independent filler, or is impregnated through the paint layer.

The system of applying a paint layer in paintings of the XVIIIth century includes three stages: coloured under-modelling, body repeated layers and the final layer with detalization. In the first half of the XIXth century coloured body under-modelling disappears, difference in thickness of paints in lights and shadows weakens, colour becomes total. Transition from multi-layer and contrasting in stroke intensity painting to an almost homogeneous enamel surface of paint layer in the beginning of the XIXth century is the most general feature of evolution of the technique of applying paint layer during the period.

The typical decay of paintings made on glue grounds manifests itself in the form of a fine pattern of cracks on the paint layer all over the painting, separate fragments consist of ground and paint layer particles tightly to each other, edges of these fragments are slightly raised, there is weak or no connection with the support, acrees are often observed (Fig. 1a). These damages are caused by processes of the natural ageing of the glue binder, and sometimes by concomitant processes of microorganisms activity.

The aged structure of paintings belonging to this group, is characterized by stiffness, low strength and water receptivity.

As to the group of paintings made on double-layer grounds, one can often observe the reduction of contact between layers of the ground, caused by the lower glue layer decay; fragments of decayng painting consist of tightly connected paint layers and the upper layer of the ground, containing white lead paint (Fig. 1b).

Typical damages of paintings made on oil grounds are as follows: medium and heavy pattern of cracks, painting surface is damaged along the cracks, deformations are cup-shaped, sections of the paint layer are tightly connected with the ground and canvas (Fig. 1c). Oil and double-layer grounds do not virtually respond to changes in temperature and moisture regime while the canvas itself is constantly changing under these conditions, that is why in the case of rapid humidity changes there appear swellings of the paint layer tightly connected with the ground (in the case of oil grounds) or with the upper layer of the ground (in the case of double-layer grounds) on paintings of this type.

The aged structure of paintings belonging to this group is characterized by extreme stiffness, tight connection between all elements of painting and low hydrophoby.

2. The investigation of laws of decay of paintings belonging to different types in conditions of accelerated heat and moisture ageing.

The abovedescribed damages of paintings made on three different types of grounds, were modelled in the process of accelerated ageing of samples, imitating separate elements of painting (ground, paint layer and varnish) and their combination. The ageing of grounds of three types: glue, oil and double-layer - was studied; a paint layer containing ochre and white lead paint was applied to grounds of all the three types; paints were covered with mastics and oil varnish. Samples placed on model looms, measuring 120 x 50 mm, had been kept in a hydrostat at 20, 40 and 60°C and 100% humidity in the darkness until signs of decay appeared. The results of these tests are presented in Fig. 2 and can be described as follows:

- under high humidity at temperatures lower than 45°C all the elements of painting (canvas, paint layer and grounds of all three types) are subjected to intensive bioaffection. As one could have expected, the most vulnerable elements in this case were glue grounds; a paint layer applied to a glue ground, makes the time of biodecay appearance almost double; the activity of microorganisms can be suppressed only at temperatures exceeding 60°C, under these conditions the binder removes almost completely, and there appear damages the character of which coincides



with those observed in real paintings: white lead paint sections get covered with fine pattern of cracks, ochre sections - with heavier peeling with slightly raised edges; fragments of the paint layer with ground remains get separated from the support; varnish protects painting against moisture, thus increasing almost by 20% the period of time till the moment of decay signs appearance.

- for samples, modelling painting on oil grounds, the character of the decay signs appearance considerably differed from the previous variant: at temperatures lower than 40°C and 100% humidity, the degree of bioaffection was much weaker than in the case of glue grounds, though one could still observe mould formation; in the case of equal time spent at 20°C and 100% humidity, the surface of painting on glue grounds gets affected almost completely, while the affected section on samples with oil grounds does not exceed 20% of the surface; at high temperatures (60°C) almost no biodecay occurs on oil grounds, however, its signs appear in the process of samples drying, due to unfavourable conditions of removing moisture from the painting layer volume; yellow spots and heavy cracks appear on white lead paint sections, however, all painting elements remain connected with the canvas.

Thus, damages of the painting layer of model samples, that appeared in the process of accelerated heat and moisture ageing, coincide with typical decay of paintings under natural conditions and have been caused exactly by technical and technological features of the structure of paintings, and, mainly, the ground.

### 3. Correction of traditional methods of restoration with regard to painting techniques.

Traditional methods of restoring oil paintings widely used by the Russian restoration school, include the following stages: canvas stretching on a loom; coating of the entire painting surface with fish (sturgeon) glue solution, containing honey as a plastisizer, PCFN as antiseptic and pinene or xylene for improving diffusion properties of the glue, this operation is accompanied by applying heat and pressure; painting lining on a new support. If it is necessary to remove deformations, traditional methods suggest that working (paper) edges should be moistured and simultaneous stretching of the loom by means of planks removal should be made, and in some cases - slight facing moisturing. This method can be applied to any type of ground, however, it does not allow us to remove effectively stable deformations caused by the aged paint layer decay.

In the framework of this report changes in methods applied only to the interaction between painting structure elements and moisture in accordance with different water repellency of ground types in question. The results of this study have shown that the abovementioned method of removing deformations by means of total moisturing canvas of a painting (1) produces a positive effect and is safe only for paintings made on glue grounds, in the case of which it is easy to remove moisture after the processing is over. At the same time such a technique increases efficiency of further impregnation with fish (sturgeon) glue. Several variants of moisturing are put forward: 1. A water soaked and wrung out piece of cloth, equal to the size of a painting, is accurately spread on a table, or dry cloth is stabilized on a separate loom and moistured by means of a pulverizer; the painting, fixed on a loom with extension planks, is placed on the cloth, the paint layer being outside (a gap should be left between the cloth and the painting), the front of the painting is covered with a polymer film; when moisturing the cloth a restorer gradually slides apart the planks of the loom, straightening the canvas. After the process of stretching is over stabilization is accomplished by an open or closed method. 2. A water soaked tissue-paper is placed all over the front of the painting so that the paper should cover the paint layer surface completely; the tissue-paper is covered by a dry filter paper of the same size and pressed. At certain intervals press is released and loom planks are being slid apart, after which the entire surface of the painting is glued up with mikalent paper, and the fixed sections are gradually covered by sized tissue-paper and ironed. 3. Moisturing can be applied directly to the back of the painting by means of a pulverizer (1) at a rate of 50 cm<sup>2</sup> of liquid per 1 m<sup>2</sup> of canvas, water may be combined with solvents, for example, with alcohol (1:10). All these methods of removing deformations by means of moisturing were effectively used for restoring paintings made on glue grounds, however, they cannot be applied to paintings on oil and double-layer grounds with

imprimatur. In the latter case a special method involving the application of heat to both (face and back) sides has been worked out for fixing the painting.

Our investigations have shown that when accomplishing lining on a new support, it is also necessary to take into account the type of the ground. Standard methods of lining yield wonderful results for paintings on glue grounds. Wax and resin masses and lately - synthetic adhesives, are still used in other countries for reproducing paintings on oil and double-layer grounds (2). Attempts to accomplish reproduction by means of fish glue are accomplished by intensive impregnation of the painting with glue and extreme increase of its stiffness. In this case there is a danger of bioaffection of paintings in the process of drying due to a slow removal of moisture. In our opinion, a method of cold reproduction involving the use of synthetic adhesives is the most promising for these types of paintings (3).

One should bear in mind that, if not in the case of heavy decay, the operation of reproduction is undesirable, especially in those cases, when the back side of the painting contains manuscript texts or drawings having a historical or scientific value. We have worked out a method of fixing painting without reproducing it, by means of covering the back side of the canvas with temporary polymer layer which prevents glue leaking behind the painting on to its back side in the process of fixing, and which can be easily removed when the process of restoring is over. Temporary polymer coating includes elastomeric adhesive produced by state industrial enterprises and represents a solution of natural rubber in gasoline or ethyl acetate. In order to obtain the most close contact between the polymer coating and canvas cloth, the glue is applied to the back side of the canvas stage by stage: no less than five layers of glue with an interval of 1 hour after applying the previous layer. To achieve better distribution of glue and to ease polymer film removal, it is useful to add gasoline solution of beewax. In 24 hours, all operations being part of standard technique are accomplished; after the process of restoring is over the temporary polymer coating is removed by small sections with the help of a plastic palette knife.



## SUMMARY

In order to protect the original colour layer the removal of overpainting with organic solvents is contraindicated. Therefore a new multienzyme preparation isolated from Antarctic krill (*E. superba*) was used. Unlike the common industrial enzymes this natural mixture, containing both endo and exopeptidases, ensures an extensive break-down of complex proteinous substrates to free, water soluble amino acids. The application of krill enzymes gave excellent results: the overpainting as well as varnish residues were rapidly removed, while the original oil-based colours remained intact.

Photo 1



Photo 2



## ANALYSIS AND CONSERVATION OF THE PICTURE "RUDOLPH II" BY G. ARCIMBOLDI.

Frantisek Makes  
Skokloster Castle  
Sweden

Description of the picture

The portrait of the emperor Rudolph II, known also as "The Gardener", was painted by the Italian artist Giuseppe Arcimboldi (1527-1593). The painting hung in Skokloster Castle, which lies 70 km northwest of Stockholm, Sweden. It is painted on an oak panel (705 x 575 mm). The original ground layer contains proteins and lipids, while the upper colour layer contained only oil. The following original pigments were found: azurite, white lead, leads yellow, malachite, vermilion, red lack and blacking. The whole picture had cracks in some areas, the colour layer was lacking. The lower part of the picture was damaged and overpainted (brown proteins varnish). The overpainting consisted of egg, oil and Canada balsam and contained the following pigments: zinc oxide, an imitation of vermilion, a red lack, chrome oxide, cadmium, blacking and ochre. This overpainting was not soluble in organic solvents. A mechanical removal of the overpainting was impossible, because the original colours were fragile, while the overpainting layer was very hard. Written information on earlier conservations of this picture, if any, is unknown. However, several recent overpaintings were detected (Photo 1).

The main purpose of this conservation was thus to remove the overpaintings. Since the overpaintings and the old brown glair varnish are not insoluble in organic solvents, they were removed enzymatically. In order to find the favourable conditions for the hydrolysis of the protein fraction of the overpaintings and, at the same time, a method of protecting the protein fractions of the original painting it was necessary to follow the proteolytic activity in the different colour layers of the picture. The actual conservation (Photo 2) revealed the painting technique with regard to the colour structure and other details. For the analysis of different colour layers and identification of the pigments and binding materials only small samples from damaged spots of the picture were sufficient.

Enzymatic removal of the overpainting

In order to remove the overpainting from the original colour layer several proteolytic enzymes were tested. The best results were obtained with enzymes isolated from Antarctic krill (*Euphausia superba*). The properties of these enzymes were earlier described by several authors (for review see Osnes 1). The enzymes, obtained by a water extraction of a frozen material were further purified by gel filtration. The preparation before gel filtration was defined as "crude", while the end product was defined as partially purified. The crude preparation, containing proteolytic carbohydrate-splitting and lipolytic enzymes, was studied first. Since the original colour layer contains both pigments and lipid constituents, the kinetics of the lipolysis were determined in order to protect the original painting.

## Method

The 2-naphtol which had been liberated by enzymatic hydrolysis of the substrate (with appropriate esters of 2-naphtol) reacted with a mixture of  $H_2SO_4$  and  $NaNO_2$ . The resulting 1-nitroso-2-naphtol was reduced on a mercury drop electrode thus, a wave proportional to the enzyme activity. The enzymatic activity was expressed as  $\mu\text{mol}$  of substrate/sec. where 1  $\mu\text{mol}$  1-nitroso-2-naphtol (173 $\mu\text{g}$ ) corresponds to 1  $\mu\text{mol}$  of substrate, i.e. 186 $\mu\text{g}$  2-naphtyl acetate, 345 $\mu\text{g}$  naphtyl myristate and 224 $\mu\text{g}$  2-naphtyl phosphate.

Table 1. Lipolytic activity in crude krill preparation

Enzyme	Substrate	Concentration	Activity
Esterase	2-naphtyl acetate	$5.10^{-3}$	0.26 $\mu\text{mol}/\text{min}$
Lipase	2-naphtyl myristate	$5.10^{-3}$	0.34 $\mu\text{mol}/\text{min}$
Alkaline phosphatase	2-naphtyl phosphate	$5.10^{-3}$	0.46 $\mu\text{mol}/\text{min}$
Acid phosphatase	2-naphtyl phosphate	$5.10^{-3}$	0.52 $\mu\text{mol}/\text{min}$
Arylsulfatase	2-naphtyl sulphate	$5.10^{-3}$	0.40 $\mu\text{mol}/\text{min}$

The phospholipase activity was reported elsewhere (2).

Table 2. pH optimum

Enzyme	pH	Buffer
Esterase	8.0	phosphate
Lipase	7.5	phosphate
Alkaline phosphatase	9.5	carbonate
Acid phosphatase	5.2	McIlvaine
Arylsulfatase	7.5	phosphate

However, the purified preparation does not contain lipolytic enzymes and should be therefore considered as nearly exclusive potent proteolytic enzyme mixture. This preparation was thus used for further efficient removal of the over-painting, varnish and cement.

## Method

The protein hydrolysis was studied by liberating  $H_2$  from break-down protein products in ammonia solution of 0.001M  $CoCl_2$ , 0.1M  $NH_4Cl$ , 0.1M  $NH_3$ . The enzymatic activity was expressed in mg of protein/min.

Table 3. Peptide hydrolase activity in a purified krill enzyme preparation:

Substrate	pH	Buffer	Temperature ( $^{\circ}C$ )	Activity
Egg-white varnish	7.5	phosphate	20	0.019

## The pH optimum of a crude krill enzyme preparation

The enzymatic activity was studied at  $20^{\circ}C$  in a sample taken from the colour layer at different pH during 20 min (Fig 1).

## The temperature optimum of a crude krill enzyme preparation:

The temperature optimum for the enzymatic activity in the colour layer as substrate was established between 45 and  $50^{\circ}C$  (enzymatic activity was expressed after incubation during 30 min), Fig 2.

Fig 1

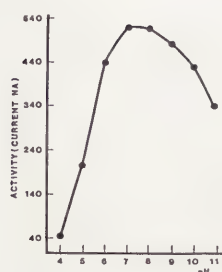


Fig 2

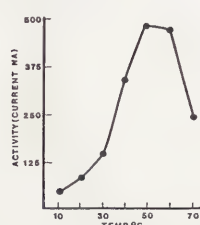
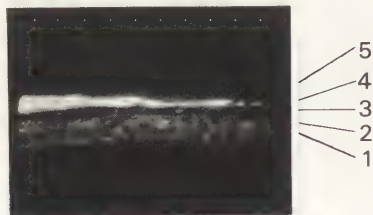




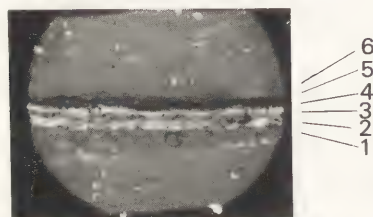
Photo 3



Green leaf

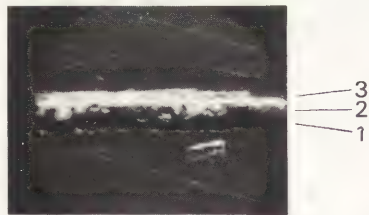
1. ground layer
2. ground layer
3. green layer
4. yellow lead, malachite
5. varnish

Photo 4



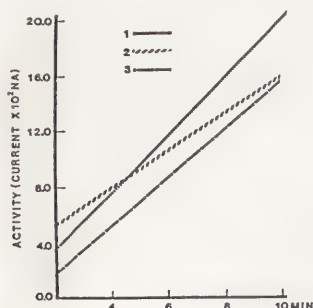
1. ground layer
2. ground layer
3. white lead
4. vermilion + little black
5. red lack
6. varnish

Photo 5



1. ground layer
2. ground layer
3. colour layer  
(after enzymatic hydrolysis  
during 2 min)

Fig 3



### Painting technique

The enzymatic hydrolysis was investigated in a cross section through the colour layer. Some samples (0.05mg) were taken with average dimension of 0.1 x 0.5 mm. They were put into resin, (Photo 3). The colour layer consists of different layers with various composition. From the cross section through the colour layer it appears clearly how the panel was prepared before painting. When the panel was isolated, it was further coated with two layers which have almost the same composition. They contain white lead, chalk and powdered charcoal. The binding-medium consists of animal glue and same parts of lipids. Both layers were isolated by a layer of a white colour which appears quite unclearly in the cross section through the colour layer. The size of the stratification varies quite considerably, as it is seen on the X-ray pictures. The last colour layer (Photo 3 and 4) has been demonstrated to consist sometimes of one or two layers. The original varnish of the picture has not been found.

Photo 5

A cross section through the colour layer from a detail of the picture representing a light green leaf. The cross section was hydrolysed by purified krill preparation in a phosphate buffer (pH 7.5, 20°C during 2 min).

The photo shows that the first ground layer was completely hydrolysed, [1] while the second one only demonstrated a partial hydrolysis [2]. Thus, the upper layer was under these conditions unaffected [3].

### Ground layer

#### Method

Prolin and hydroxyprolin occurring in the mixture of amino acids extracted by hydrolysis of proteins present in the ground layers and in the cement were analysed with respect to the quantity of hydroxyprolin present in the above mentioned layers. The mixture of amino acids resulting from the protein hydrolysis was nitrated with  $\text{HNO}_2$ . Under these conditions the amino acids together with the primary amino groups were transformed into hydroxyacids, but only prolin and hydroxyprolin were transformed into nitrosamines. The mixture of nitrosamines was then separated chromatographically (3).

Fig 3

shows the hydrolysis rate reaction in both ground layers and in the glair varnish. The difference in hydrolysis rate in the two ground layers may be explained by the differences in the protein lipid content.

#### Curve 1

Some residues of an old glair varnish which was found under the overpainting. This varnish was brownish yellow and extremely hard, but could be easily removed after enzymatic hydrolysis during 3 min.

correlation coefficient	+ 0.981
standard deviation	+ 1.329
intercept	- 2.257
slope	+ 2.280

Curve 2

The second ground layer of the panel.

The binding-medium in this layer is glue and oil. They were found in other proportions than those in the first ground layer.

correlation coefficient	+ 0.850
standard deviation	+ 2.464
intercept	+ 2.395
slope	+ 1.306

Curve 3

The first ground layer of the panel.

The figure 3 shows that the hydrolysis of the first ground layer proceeded slower than the hydrolysis of the varnish.

correlation coefficient	+ 0.986
standard deviation	+ 0.871
intercept	- 1.728
slope	+ 1.740

The overpaintingsPhoto 6

The presence of protein could be demonstrated in the overpainting, as well as in the old brown varnish.

Method

The proteins were analysed by a mercury drop electrode. The production of a catalytic hydrogen current on the mercury drop electrode in presence of cobalt, (a phenomenon discovered by Brdicka) was measured in a solution of proteins in different analytical applications (4).

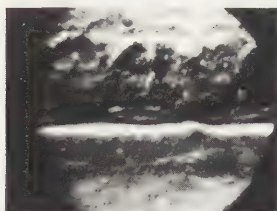
The green overpainting

The size of this overpainting consisted of egg, oil and resin. The pigments present in the overpainting were zinc oxide, chrome oxide, cadmium, ochre and a black pigment. The enzymatic removal of the overpainting did not meet with difficulties (Fig 4, photo 7), except for the red overpainting, which was difficult to remove (Fig 4).

Photo 6



Photo 7

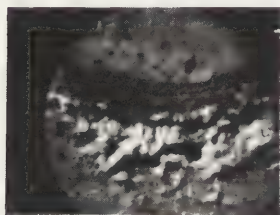


8  
7  
6  
5  
4  
3  
2  
1

Green overpainting

1. ground layer
2. ground layer
3. white lead
4. green layer
5. yellow lead, malachite
6. varnish after enzymatic hydrolysis during 1 min.
7. brown cement
8. green overpainting

Photo 8



4  
3  
2  
1

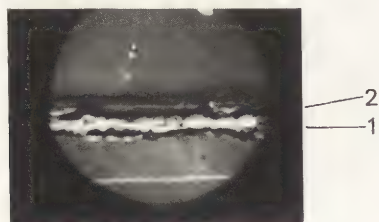
1. white cement
2. vermilion
3. varnish after enzymatic hydrolysis during 1 min.
4. red lack

Photo 8

The hydrolysis rate of the overpainting depended particularly on the overpainting composition. The easiest layer to hydrolyse was the isolation protein layer. The first layer of the original picture was situated between the original colour layer and the overpainting. It was found only in the form of residues of an old protein varnish which was very hard and bronze-coloured. Moreover, the protein present in the isolation layer of the overpainting separated the vermilion from the red lack (Photo 8).

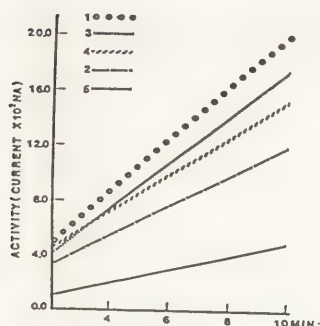


Photo 9



1. ground layer  
2. colour layer  
(after enzymatic hydrolysis  
during 10 min)

Fig 4



### The colour layer and the ground layers

Lipids and proteins were present in different concentrations in nearly all the colour layers of the picture. The first colour layer, however consisted only of lipids [2]. The ground layer was hydrolysed very little by the enzyme [1]. The lipid (oil) component in the colour layer was studied by lipolytic enzymes (Photo 9).

Fig 4

The hydrolysis rate of the white (Curve 1), and brown cement (Curve 4), red overpaintings consisting of two layers (Curve 2 and 5), and the green overpainting (Curve 3).

white cement:	correlation coefficient	+ 0.998
curve 1	standard deviation	+ 0.365
	intercept	+ 0.685
	slope	+ 2.157

brown cement:	correlation coefficient	+ 0.998
curve 4	standard deviation	+ 0.229
	intercept	+ 1.542
	slope	+ 1.478

red overpainting 2:	correlation coefficient	+ 0.993
curve 2	standard deviation	+ 0.394
	intercept	+ 1.023
	slope	+ 1.279

red overpainting 1:	correlation coefficient	+ 0.977
curve 5	standard deviation	+ 0.382
	intercept	- 0.544
	slope	+ 0.600

green overpainting:	correlation coefficient	+ 0.981
curve 3	standard deviation	+ 0.940
	intercept	+ 0.805
	slope	+ 1.776

### The restoration

The whole painting had cracks caused by the changes of the relative air humidity in Skokloster Castle. The cracks caused by the activity of the panel, covered the whole surface of the picture. The material of the panel (wood) reacts to changes in the relative air humidity by stretching and shrinking. The movements which arise in this manner cause a tension between the ground layer and the panel (Photo 10).

From the analysis of the colour layer and the proposed removal of the overpainting it appeared that the krill enzymes, used for removing the overpainting, should not be allowed to reach the ground layer of the original picture. The ground layer was therefore preserved from the spreading enzyme by impregnating the painting from the front side with a mixture of wax, resin and an organic solvent at 40°C. In this way, all cracks where the enzyme could spread in to the ground layer were filled. The overpainting was removed by the purified krill enzyme preparation mixed with polyethylene glycol in a phosphate buffer at pH 7.5, forming a thick paste. This process was terminated after 10 min, according to previous investigations (Photo 11).

There was a problem with the removal of overpainting of red flowers and greens. The presumed hydrolysis rate of the proteinaceous component of the overpainting accorded with the results of the tests in the upper layer which contained a red varnish and cement. However, the calculated hydrolysis rate did not accord with the results in the lower layer of the overpainting which consisted of a mixture an imitation of vermilion and of the medium. As the tests showed, the upper layer of the overpainting with the varnish contained more medium than pigments in contrast to the lower layer where the pigments dominated. It was also remarkable that both layers were separated by a proteinaceous isolation layer.

Moreover, the tests showed that eosin was present in the vermilion imitation, causing inhibition of the enzymatic activity. Thus, it was necessary to change the procedure for the removal of the lower layer of the red overpainting. This was removed in a following way: before the enzyme, removal the layer was damped with acetone and the section which was dissolved in acetone phase was absorbed by a filterpaper. After the layer was dried, the

Photo 10



Photo 11



hydrolysis was carried out with a crude krill enzyme preparation (containing lipolytic activity). The last residues of the overpainting were removed by purified krill enzyme preparation (without lipolytic activity). In order to protect the areas of the picture where the overpainting had already been removed, the original colour layer was covered with wax with dammar harts. Finally, the panel was impregnated on the back side with a mixture of bees wax and dammar harts to prevent it from humidity. Then the picture was cemented and retouched on the damaged areas. Slightly damaged areas were repaired by gouache, while on the larger areas the retouch was performed by a fine hatching. The painting was at last coated with a final varnish that looks like wax and resin.

#### References

1. Osnes KK (1985) Peptide hydrolases of Antarctic Krill, *Euphausia superba* PhD-thesis, Trondheim, The Norwegian Institute of Technology
2. Kolakovska A (1986) Lipid composition of fresh and frozen-stored krill *Z Lebensm Unters Forsch* 182, 475
3. Makes F (1979) Enzymatic consolidation of Paintings. PhD-thesis, University of Göteborg
4. Makes F (1984) Damage to old bookbindings in the Skokloster library. A new method of inhibiting injurious enzymes in leather. *Skokloster studies*, 17



# Working Group 3

Ethnographic Materials

Matériaux ethnographiques





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Regional Co-ordinator  
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S. Gatenby  
M. Henderson  
D. Horton-James  
N. King Smith  
S. McKendrick  
R. Norton,  
Bibliography Compiler  
M. Scott  
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Regional Co-ordinator

## TRIENNIAL OVERVIEW

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S. Walston (Australia)

## Assistant Co-ordinators

A. Howatt Krahn, Newsletter Editor (Canada)  
R. Renshaw-Beauchamp (Canada)  
P. Speroni (Denmark)

## PROGRAMME 1984-1987

1. Undertake a world-wide survey to identify the nature and extent of ethnographic conservation being carried out and to identify the special problems and needs that exist.

2. Establish a Working Group Newsletter to be published twice yearly.

3. Develop a working definition of 'ethnographic materials' for discussion and resolution at the 1987 ICOM-CC Meeting, with the purpose of defining the scope of the Working Group's activities.

4. Compile a bibliography of the ethnographic conservation literature to be made available through the Newsletter, international documentation centres and at the 1987 Meeting.

## SUMMARY

The primary aim of the Working Group during the 1984/87 triennial period has been to develop an information and communication facility for people involved in the conservation and curation of ethnographic collections. Ethnographic conservation is a field where people tend to be isolated and information fragmented and hard to find. Collection and materials diversity, language, distance and lack of specialized training and literature have all contributed to the slowness with which ethnographic conservation has developed and been recognised as a specific discipline.

The first priority has therefore been to locate people and information concerned with the conservation of ethnographic material and at the same time establish an international communication network through which information can be exchanged.

A first step has been made towards achieving this objective with the successful completion of the Group's three-year programme. A Newsletter is now published twice yearly with contributions produced in both the authors' preferred language and English.

460 ethnographic conservators have been contacted in 43 countries and 40 Regional Co-ordinators appointed. The results of the International Ethnographic Survey have been collated and distributed and the Bibliography of Works on Ethnographic Conservation has been completed. In addition, an Interim Meeting of the Working Group has discussed the scope of ethnographic conservation and considered new initiatives. Numerous informal meetings have also taken place between the Co-ordinator, Newsletter Editor and Regional and Project Co-ordinators which have been invaluable in the successful planning and implementation of the programme.

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## SUMMARY

The physical and chemical properties and working characteristics of a silicone rubber/microballoon mixture as a gap-filler for wooden objects are described. The application to cracks in objects involves preparation of the surface, mixing of the fill material, finishing and inpainting. A caution is expressed with regard to the use of silicones on absorbent surfaces.

## A SILICONE RUBBER/MICROBALLOON MIXTURE FOR GAP FILLING IN WOODEN OBJECTS

R.L. Barclay, Senior Conservator, Ethnology  
D.W. Grattan, Senior Conservation Scientist, Conservation Processes Research  
Canadian Conservation Institute,  
1030, Innes Road, Ottawa, Ontario K1A 0M8, Canada

## 1. Introduction

A wide range of materials is available to the conservator for the filling of obtrusive cracks in decorative wooden objects. Hitherto, gap filling materials commonly used fell into five broad categories:

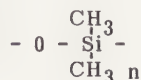
- animal glue based binders
- plasters
- waxes
- resins
- oils

All the above might contain particulate or fibrous extenders and pigments, and mixtures of materials from these categories are not uncommon. All these materials have three basic characteristics: ease of application, ease of finishing and inpainting, and relative inelasticity. It is this latter characteristic which led the authors to investigate alternative materials which might possess more desirable mechanical properties (1). Clearly, if a crack is to be filled for aesthetic reasons, the fill must resist the movement of the wood as little as possible, and be elastic enough to return to its original shape. The ease of working the material during application should be a comparatively minor consideration when planning the long-term welfare of the object. None of the many fill materials alluded to above possess this elastic property, although several deform readily under pressure, and the effect of cycling humidity is evident on many wooden artifacts where inelastic fills have been used. With fills of a compression modulus significantly higher than that of the wood, irreversible damage can occur during compression (Fig. 1), while with fills of low modulus the material itself can be crushed and extruded.

The silicone elastomers appear to possess desirable mechanical properties, having a low modulus of compression while still being highly elastic.

## 2. The Silicone Rubbers

The silicones have been used in industry since at least the 1940's (2) but their consideration as potential conservation materials is comparatively recent. The two silicone rubbers discussed here, Dow Corning 734 RTV and Dow Corning 738 RTV, are both poly (dimethyl) siloxanes where the chief chain building unit is dimethyl silicone,  $[(CH_3)_2SiO]_x$ . This is often shown as follows:



The cure chemistry of these two RTV resins differs significantly. 734 RTV cures by acetoxy cross-linking, and acetic acid is produced as a by-product. 738 RTV, one of the non-corrosive silicone rubbers, has cross-linking via alkoxy groups where the by-product is methanol. In both cases the polymerization is initiated by reaction with atmospheric moisture.

The acetoxy-curing silicones have been found to be the more reliable by the present authors, as they have a much longer shelf life, but the emission of acetic acid could be detrimental to the materials upon which they are used. On the other hand, the alkoxy-curing silicones, although less reliable in terms of specified curing rates, have the advantage of being quite innocuous. Experiments have been conducted with both kinds and no marked difference in their working characteristics was found, provided it was possible to use fresh material. The manufacturers and distributors of these products will provide information on batch marking on request.



- 1) Although some shrinkage of fill is responsible for the gap seen here, it is likely that the wood cells at either side have been crushed.

### 3. Microballoons and Bubbles

Bakelite Phenolic Microballoons are produced by the Union Carbide Corporation. Bakelite is a registered trade mark of Union Carbide, and the term "microballoons" is a registered trade mark of Emerson and Cuming Inc. Phenolic microballoons range in size from 0.0002" (0.005mm) to 0.005" (0.125mm) and have an average particle size of approximately 0.0017" (0.043mm). They are reddish/brown in colour. The type described here are BJO-0930, the less dense of the two ranges offered (3). The Glass Bubbles described here are 3M Inc., type B23/500 (4) and range between 0.001" (0.025mm) and 0.006" (0.15mm) in diameter, and are white in colour.

Microballoons are customarily incorporated into resins to alter their flow characteristics, to render them easier to apply, to make their application economical, and to allow them to be worked when cured. Phillips and Selwyn (5) describe their use in patching compounds for wood repair in historic buildings. Both phenolic microballoons and glass bubbles have been used as extenders for silicone rubbers by the present authors and no significant difference in application, aside from the obvious colour, was noted.

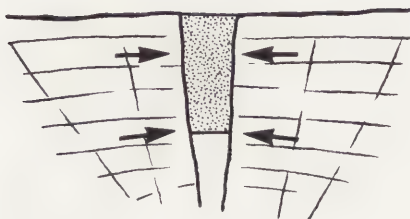
### 4. Silicone Rubber/Microballoons Mixture

The application of mixtures of silicone elastomers and microballoons for filling cracks in wooden artifacts has been previously described (6,7) and it appears that these mixtures incorporate the desirable properties of the silicones with few of their disadvantages.

The advantages of these fill materials are as follows:

- Because they have no carbon-to-carbon bonds the silicone rubbers are extremely stable polymers, and are completely inert when cured.
- Although silicone rubbers have a very high surface energy, and are therefore water repellent, they are very permeable to moisture.
- The silicone rubbers are highly elastic and have a low compression modulus - they distort very readily under pressure, but return to their original shape when pressure is released. Similarly, if good bonding is achieved between fill and substrate, the rubber will stretch.
- Extending the silicone rubber with large quantities of microballoons produces on curing a so-called syntactic foam. The freshly mixed material is a workable paste which can be shaped and moulded. The spherical shape of the microballoons or bubbles allows for a high degree of packing coupled with good flow characteristics.
- Because the ratio of silicone to microballoons is so high the resultant surface is carvable and sandable in a way which would be impossible on pure silicone rubber.
- Exposure of microballoons during carving and sanding creates a surface with sufficient "tooth" for inpainting.

The chief disadvantage of using a silicone fill on a wooden object is the tendency of uncured silicone to migrate into the wood rendering future treatment difficult. Portell (8) has described the silicones as "...excellent adhesives..." However, Fogel (9) reports that fills made of a mixture of silicone resin and glass microballoons could be easily removed mechanically, and the present authors have also noted the easy peelability of cured fills. It is apparent that the extending with microballoons, aside from enhancing the working properties of the rubber, markedly decreases the adhesive quality; by producing a workable paste the substrate is no longer presented with a significant surface area for penetration and adhesion. Tests on the adhesion of fills to wood substrates conducted by Fuller (10) have supported this. However, it is clear that even a heavily loaded paste of silicone resin and microballoons will leave traces of silicone on the wood to which it has been applied. This is easily demonstrated by allowing the mixture to cure on a flat wood surface, peeling it off, and then attempting to draw with ink on the newly exposed surface. In view of this, it is considered necessary to apply a resist to the wood parts to be filled before applying the mixture.

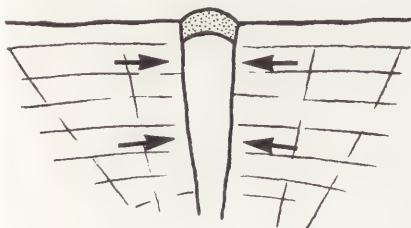


### 5. Application

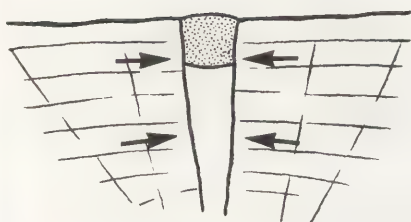
Usually when cracks or losses are being filled the object is to present an unobtrusive surface, and the fill is rarely called upon to provide mechanical support. It is therefore neither necessary nor desirable to extend the fill too deeply into a crack. Indeed, if the fill is too deep in relation to its width, its elastic properties will be severely constrained by its geometry (Fig. 2). On the other hand, a

- 2) If the fill is too deep in relation to its width it will be prevented from distorting when under pressure.





- 3) If the fill is too shallow it will buckle rather than compress under pressure.



- 4) Ideally, the fill should present a square cross-section.

shallow fill over a void will tend to buckle rather than compress under pressure (Fig. 3). A square cross-section, where the depth of fill is equal to its width, will represent an ideal situation (Fig. 4). In order to achieve this, it is necessary to first insert into extensive cracks an easily deformable substance which will act as a base for the fill material. Fogel (11) described the use of a layer of compressed acid-free tissue for this purpose, while the present authors have found that individually fitted pieces of low density (1 lb/cu ft : 0.002 gm/cc) polyethylene foam (Ethafom) are very effective (12).

In order to prevent the possible migration of silicones into the wooden substrate, a resist is applied. A number of synthetic resins are available for this, perhaps the most easily removable being the ethyl and methyl celluloses. A solution of 2% Ethulose (ethyl hydroxy ethyl cellulose) in water is applied to the area to be filled and allowed to dry. A second coat is applied gently to the first and also allowed to dry. This resist has the additional advantage of somewhat retarding penetration of acetic acid from the acetox curing silicones, although a less permeable resist would be preferable for this if it is considered a problem. (In fact the pH of the silicone resin, approximately 3.5, is not significantly lower than that of fresh hardwood.)

To enhance adhesion of fills in shallow depressions or extensive surfaces a thin layer of the silicone resin (without microballoons) may be applied with a brush directly to the coated wood, and allowed to cure before the fill mixture is applied. This has a similar effect to Dow Corning's Prime Coat 1200, which is manufactured for this purpose. Tests have shown that the resist layer of Ethulose effectively resists penetration of the silicone but provides fair adhesion between fill and substrate.

As an additional precaution against contamination of the unfilled area with silicones, the sides of the fill are masked with self-adhesive drafting tape. On sensitive areas, which might be damaged by this masking, a coat of Ethulose could be applied temporarily.

A mixture of between 3 and 2.5 parts to one by weight of 734 or 738 RTV and phenolic microballoons or glass bubbles produces an easily workable paste or putty with fair adhesive properties. Mixtures of a lower ratio tend to lose cohesion, although Fogel (13) reports using a 2:1 mixture. Clearly, a personally preferred mixture can only be arrived at by experimentation. It is important to note that in a relative humidity of 50% the first stage of curing can occur in only 10 minutes, after which the material is no longer workable. Speed of application is essential and only small quantities should be made up as required. It is therefore preferable to over-fill cracks and voids and rely upon carving to achieve the final shape, rather than attempting to contour the surface accurately during application (Fig. 5).

Powder pigments may be added to the mixture to provide a suitable base colour for inpainting, although loading with pigments will affect the working properties of the paste and will require adjustment of the quantities of microballoons used. Obviously the brown phenolic microballoons are of limited value unless a fully opaque inpaint is to be used. Glass microballoons in the mixture tend to lighten the colour value of added pigments.

Full curing of a 1/8" (3mm) cross-section takes 24 hours and full mechanical strength is achieved after 7 days. (However, addition of phenolic microballoons tends to accelerate curing, at least in the acetox curing silicones.) Fills are easily workable the day after application. Carving is most easily done with a scalpel, although woodworking tools may be used provided that the angle of attack is very shallow. Chisels and gouges need to be ground to an angle of less than 10°, with little or no honing edge. (This makes the cutting edge of the tool too weak for use in woodwork, so a separate set of tools will be required.) The fill may also be sanded quite effectively, although at a mixture ratio of 3:1 some resistance and microscopic tearing may be encountered. The more densely loaded fills have superior sanding qualities at the expense of cohesion and adhesion.

Inpainting has been carried out successfully with solvent-based acrylic paints (Fig. 6) but watercolours with a suitable surfactant such as ox gall are also successful, provided that the base colour is close. Thick watercolour has a tendency to crack under deformation of the rubber substrate. As the fill is inately flexible, and is chosen primarily for this characteristic, it is desirable to have an equally flexible colour film. While solvent-based acrylics and thinly applied watercolours have shown a fair degree of flexibility, a mixture of 738 RTV and dry pigments diluted with mineral spirits has been used successfully (14). This produces a smooth, glossy film which can be matted while tacky. This technique is well suited to fills in solid areas of colour, but would probably be less successful on more



- 5) Filling of a crack with 738 RTV and phenolic microballoon mixture. Note the polyethylene foam base in the crack and the masking tape at both sides.



6) The carved fill in-painted with solvent-based acrylics.

intricate designs. For fills on furniture a thin film of 734 RTV diluted with mineral spirits has been applied over inpaints to achieve gloss, although it cannot be wax polished. The inpainting technique chosen depends largely upon the kind of surface to be reproduced and the preference of the operator.

#### 6. Conclusion

The material described here represents a departure from current practice, but its application is based on the premise that low modulus of compression and high elasticity are the primary requirements of a fill material for wooden objects, especially those that will be exposed to cycles of relative humidity. The silicones have been rightly regarded with some suspicion by conservators (15), due in part to their low solubility and high surface energy, both of which factors make their presence in artifacts undesirable. They are initially difficult to remove, should the need arise, and their continuing presence can be a deterrent to future treatment. However, if these properties are kept in mind, and the material is applied with the necessary precautions, a silicone rubber and microballoon mixture surpasses fill materials in current use, particularly in terms of the chief criterion, flexibility.

#### 7. Suppliers

##### 734 RTV and 738 RTV

Dow Corning Corporation, Midland, Michigan 48640, U.S.A. or local suppliers.

##### Phenolic Microballoons:

Union Carbide Corp., 270 Park Ave., New York, NY 10017, U.S.A., or local supplies.

##### Glass Bubbles:

3M Company, 2501 Hudson Drive, St. Paul, Minnesota, 55144, U.S.A., or local suppliers

##### Solvent-based Acrylic Paints

Bocour Artists' Colours Inc., New York, NY 10019, U.S.A.

Ethulose E-400: Chemaster Corp., Long Island City, N.Y. 11103, U.S.A.

#### 8. Acknowledgements

The authors would like to acknowledge the assistance of all the conservators who provided suggestions for fill materials to be tested, and also all those who responded to our request for input in the IIC-CG Newsletter. We would particularly like to thank John Perkins, Jean Portell and Natalie Firnhaber for their interest.

#### 9. References

- 1) Grattan, D.W. and Barclay, R.L., "A Study of Gap Fillers for Wooden Objects", Studies in Conservation, (in preparation).
- 2) Rochow, E.G., An Introduction to the Chemistry of the Silicones, John Wiley and Sons, New York, 1951. 2nd edition.
- 3) Union carbide Corp., Product Application Bulletins.
- 4) 3M Inc., Technical Bulletins.
- 5) Phillips, M.W. and Selwyn, J.E., Epoxies for Wood Repairs in Historic Buildings, U.S. Department of the Interior, Washington D.C., 1978.
- 6) Grattan, D.W. and Barclay, R.L., "Gap Fillers for Wood", International Institute for Conservation - Canadian Group Newsletter, December 1984.
- 7) Fogel, S., "Project Data for a Filling Mixture and a Paint Made from 738 RTV Silastic", distributed with "Interior Totem Poles", Poster Session, American Institute for Conservation, Washington D.C., 1985.
- 8) Portell, J., Personal communication to authors, January 1985.
- 9) Ibid 7.
- 10) Fuller, R.D., "An Investigation of the Physical and Tensile Properties of Selected Elastomeric Gap Fillers for Wood", Master of Art Conservation Thesis, Queens University, Kingston, Ontario, 1985.



9. References

- 11) Ibid
- 12) Ibid 6.
- 13) Ibid 7.
- 14) Ibid
- 15) Portell, J., "The Persistence of Silicone Polishes", American Institute for Conservation Specialty Group Abstracts, Washington, 1985.





## SUMMARY

Research was carried out to establish the feasibility of cleaning Maori feather cloaks ultrasonically in aqueous solutions. Using the results of earlier work on the effects of ultrasonic action upon feathers, species decorating cloaks and associated fibres making up the cloaks, were identified as being either suitable or unsuitable to be subjected to ultrasonic action. At the same time observations were made as to the efficacy of standard washing treatments for cloaks carried out in the past. Comparing the various results on a scanning electron microscope allowed the best assessment to date on what happens to feathers and fibres under various cleaning procedures. The research has established that 9 of the 11 feather species found in the cloak collection at Auckland Museum can be cleaned with ultrasonic action. Also all fibres except black coloured flax fibre can be cleaned in the same conditions as feathers. Despite their differing physical and chemical properties these composite material garments can be safely washed in water using ultrasonic action as a standard part of the cleaning procedure.

## AN INVESTIGATION INTO THE ULTRASONIC CLEANING OF NEW ZEALAND MAORI CLOAK MATERIALS

Gerry Barton and Sabine Weik  
Conservators  
Auckland Museum  
Private Bag  
Auckland  
New Zealand

## 1. INTRODUCTION

An aspect of ethnographic conservation in New Zealand museums which has required close attention for some time is that concerning the cleaning of Maori cloaks. Encouraged by the results we observed when exploring the use of ultrasonic cavitation in the cleaning of feathers used to decorate Maori weaponry and domestic objects<sup>1</sup> we decided to extend the tests to include all materials used in the fabrication of Maori cloaks held in the Auckland Museum collection in an attempt to establish whether cloaks requiring cleaning could be washed under similar conditions<sup>2</sup>.

The tests were designed to establish several things and were based on the assumption that the less time the cloaks were immersed in their washing bath the better it would be for the garment. We wanted to see:

1. If any harm was evident when soaking the various materials used in making the cloaks for periods up to 90 minutes. Would fibres untwist? Knots swell and break quills? Would feather barbs, etc. swell and deform, matt together, lose their alignment?
2. Could the various materials withstand 2 minutes ultrasonic action?
3. Could the various materials withstand 2 minutes ultrasonic activity after 15 minutes, 45 minutes, and 90 minutes of soaking?

The results of these tests were observed with a scanning electron microscope. As a comparison to the ultrasonically cleaned samples other samples from the same feather or length of fibre were cleaned in the same detergent for a similar time. For example, two samples of a fibre would be immersed for 90 minutes after which only one of them would undergo ultrasonic cleaning. This was repeated for all samples and the results compared.

## 2. THE CLOAK MATERIALS

All materials tested were identified from cloaks in the Auckland Museum collection. Maori weavers designed a variety of cloaks the details of which have been extensively discussed in New Zealand material culture literature<sup>3</sup>. For our purposes we simplified the many types into 5 groups categorized by materials:

1. Prestige cloaks with no decoration.
2. Cloaks with tags of black coloured flax or with coloured wool decoration.
3. Cloaks with feather decoration.
4. Cloaks with dog skin decoration.
5. Rain capes comprised of untreated or roughly processed flax fibre, cabbage leaf tree, or other fibres.

The cloaks consist of a woven fibre (in reality a knotting or twining method of fabrication. However their makers are always known as weavers so for the sake of consistency of terminology rather than of exactitude the cloaks will be described as having been woven) known as a kaupapa and it is upon this substrate that the various decorative elements will be fixed.

Many cloaks have a decorative border around the sides and bottom known as a taaniko border. These are invariably geometric in design being woven of differently dyed flax fibres or of a combination of flax fibre and coloured wools.

We focused our cleaning research on the materials relating to the cloaks in the first 3 categories, the numbers of which made up about 95% of the Museum's cloak collection. Dog skin cloaks were excluded because of their rarity (meaning samples for testing were unavailable). The rain capes were ignored as none of the garments in the Auckland Museum collection require cleaning.

Having isolated the group of textiles requiring attention we then identified the various materials used to fabricate them.

## 2.1 Kaupapa Materials

1. New Zealand flax (*Phormium tenax*). This plant is in fact not a linen flax as its common name suggests but rather a perennial monocotyledon belonging to the agave family. The leaves which provide the

fibre are green, leathery and sword-shaped and when mature can be up to 3 metres in length growing in crowded fans from stout rhizomes. Maori weavers identified over 50 varieties of *Phormium tenax* useful to them.

The flax was processed in several ways to extract the fibre<sup>3</sup>. Fibre destined for the prestige cloaks appears to have been treated differently to fibre being processed for the tag and feather cloaks.

The fibre for these more common cloaks was washed several times and pounded with stones to soften and whiten it. Fibre for the prestige cloaks, according to an early account, had fewer washes than normal flax fibre and was left unpounded in order to achieve a silky sheen which was greatly valued. However another account (by the same writer but 26 years later) says that the fibre was neither washed nor pounded in order that the yellowish tint of the natural fibre should form a further distinction from the other types of cloaks<sup>2</sup>. Obviously both accounts cannot be correct and a more accurate description will have to await a scientific analysis of these fibres. Nevertheless the value of these conflicting accounts is that conservators must at least be aware that the prestige cloak fibre could possibly have been processed in a way which could preclude washing as a cleaning method.

2. Wool fibre in various colours purchased from shops in the developing colonial towns throughout New Zealand.
3. Cotton in the form of candlewick also available throughout colonial New Zealand.

## 2.2 Decoration

This is either of wool, black coloured New Zealand flax or feathers. The feathers identified on Auckland Museum cloaks and test cleaned are:

1. tui (*Prosthemadera novaeseelandiae*)
2. pheasant (*Phasianus colchicus*)
3. weka (*Gallirallus australis* & *G. hectori*)
4. domestic fowl (*Gallus gallus*)
5. peacock (*Pavo cristatus*)
6. kaka (*Nestor meridionalis*)
7. parakeet (*Cyanoramphus novaeseelandiae*)
8. guinea fowl (*Numida meleagris*)
9. kiwi (*Apteryx* spp.)
10. emu (*Dromaius novae-hollandiae*)
11. kereru (*Hemiphaga novaeseelandiae*)

As we restricted our research to the Auckland Museum feather cloak collection this list is not definitive for New Zealand. As well as the possibility of a few more species being added we have also seen a cloak in a private collection decorated with dyed fowl feathers.

The black coloured flax fibre was used extensively in taaniko borders and in the tags tied to the kaupapa of many cloaks and its use in these and other textile contexts has created the single biggest problem in the care of Maori textiles. This is because the procedure carried out in order to colour the flax usually guarantees the eventual destruction of the fibres so treated. The characteristic feature of black flax fibres is one of either crumbling and powdering of the fibres, or of their entire absence in the cloak due to their disintegration long ago.

The colouring process has been frequently described in the literature concerning Maori textiles. Briefly, flax fibres are steeped in a solution of crushed bark for 12-16 hours. When removed from this bath they are sticky and brown coloured. They are then placed in a specially selected black mud for about 24 hours whereupon they are removed, washed and dried. In the twentieth century it has been observed that when some traditional mud sources were assessed by their owners as looking a little lacklustre, iron scrape was thrown into them in the belief that this revitalized the mud. This colouring process has been described as "chemically sound", producing a completely fast colour, the assumption being that the tannic acid from the crushed bark permeates and bonds with the swollen flax fibres thus providing a chemical bridge or mordant upon which the iron salts in the black mud can attach themselves to the fibres. The limited investigations carried out on the colouring process suggest that this description is not always correct. Certainly the colour on some cloak tags and taaniko is not fast.

Tests carried out in aqueous solutions (such as pH readings) with black coloured fibres always resulted in strongly discoloured water. As regards the effectiveness of the mordant an analysis of a sample of mud by the DSIR indicated that the chemical bonding that was supposed to occur between the introduced tannic acid and the iron salts in their sample could not in fact take place, the iron content of the mud not being



in the form of iron oxide (magnetite). Instead the analysis showed that the black colour was a pigment which could only be mechanically, as opposed to chemically, fixed into the interstices of the fibres.

Whatever the chemical and physical processes involved in creating the black colour what is clear is the fact that one of the primary causes of the deterioration that characterizes these coloured fibres is the presence of iron salts in the mud. Black coloured fibre samples from a cloak and a piupiu when analysed were found to contain very high levels of iron<sup>2</sup>.

Another factor which must contribute to the disintegration of the fibres is the acidity of some of the mud baths used for the colouring. For instance a sample collected in 1984 from a bath in Rotorua had a pH of 2.9. Such an acidic environment is very bad for cellulosic material to be immersed for 24 hours. However, even this degree of deterioration will be exacerbated as such a strong acid solution will help dissolve more iron than the case would be if the mud pool were neutral or slightly alkaline.

### 3. EXPERIMENTAL

Our approach to the ultrasonic cleaning tests was governed by the results of our earlier experimentation<sup>1</sup>. These tests had determined to our satisfaction that the detergent designated "Formula B" was appropriate for the tests and that 2 minutes ultrasonic action was enough to clean our samples.

Per litre<sup>4</sup> : 1gm sodium lauryl sulphate ( $\text{RSO}_4\text{Na}$ )  
 2gm alkyl polyglycol ether  
 (non-ionic  $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$ )  
 2gm sodium polymetaphosphate  
 0.2gm carboxymethyl cellulose

By corresponding with a number of British and German conservators we were able to establish that they had approached cloak washing in much the same way as we ourselves had in Auckland Museum<sup>2,5</sup>. Generally speaking the process began with immersing the garment, supported flat on a screen, into a water and detergent bath for periods of between 45 and 120 minutes. Some mechanical action usually took place in the way of gentle wave action or prodding with the fingertips during the immersion. When washing was complete the cloak on its screen was lifted and rinsed and allowed to dry either in the ambient air or with cool air blowers being directed over the cloak. Only one institution had supplemented this method with ultrasonic action<sup>6</sup>.

With these case studies in mind we selected three immersion times to precede the ultrasonic cleaning action - 15, 45 and 90 minutes. Fifteen minutes seemed the minimum time one could realistically clean a cloak; 45 minutes because it allowed some soaking out of stains (if necessary); and 90 minutes because cloaks washed in the past have often been immersed for periods as long as this.

The feathers were obtained from mounted bird specimens in the Museum's Ornithology Department. The samples were all from the oldest bird specimens available. This meant they were usually as old as the cloaks themselves and had suffered the vicissitudes of prolonged open display, several moves to new museum buildings, and/or wear and tear from variable storage conditions over about 100 years. The flax, wool, and cotton fibres came from cloaks in the collection.

The tests were carried out in a Sonicator SC200 ultrasonic cleaner which has an operating frequency of between 40 and 60 kHz.

### 4. RESULTS

Before discussing the specific findings of the tests it must be noted the dyed flax samples fell apart in the cleaning solution whether or not ultrasonic action was introduced into the tank. Consequently these samples are not further discussed.

#### 4.1 Cleaning - Feathers

When viewed at high magnification the dirt characteristics of 9 of the 11 samples were very similar. The flat surfaces of the barbs and barbules are covered with many lumps of dirt and dust giving the surface a matt and sometimes an almost grainy appearance. The largest deposits of dirt were invariably lodged in the acute angle where the barbule springs off from the barb (figs. 1, 2 & 3). The emu and kiwi samples were less dirty and this probably relates to their more open structure. There were a lot less dirt particles on their surfaces, however, the emu feathers were unique in the sample range in that the structure of their barbules is such that quantities of dirt were contained within the barbules themselves. Emu barbules comprise in part a cellular net-like structure and the cavities created within the barbule trap a great deal of dirt (fig.4). The net-like appearance varies from barbule to barbule both in surface area and in complexity, some sections of barbules being almost all cavities while other



Fig.1 An uncleaned pheasant feather, approx. 300X mag.

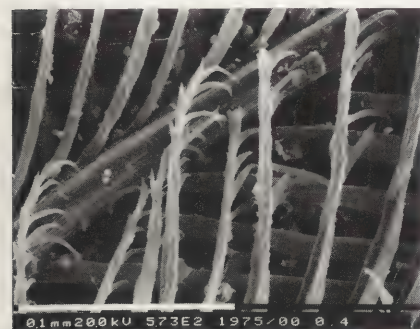


Fig.2 An uncleaned domestic fowl feather, approx. 600X mag.





Fig.3 An uncleaned guinea fowl feather, 600X mag.

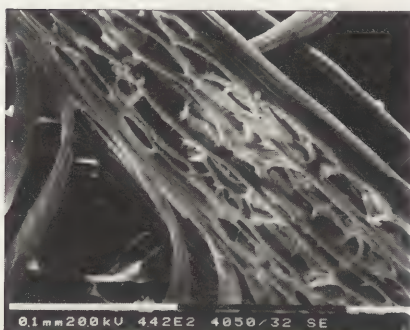


Fig.4 An uncleaned emu feather, approx. 450X mag.



Fig.5 A domestic fowl feather immersed in the washing solution for 45 minutes but not ultrasonically cleaned, approx. 500X mag. (compare with fig.2).

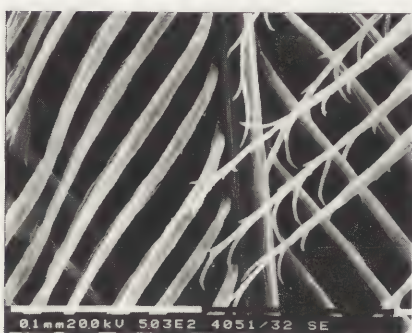


Fig.6 A domestic fowl feather immersed for 45 minutes followed by 2 minutes ultrasonic cleaning, approx. 500X mag.

areas are smooth in the same way as barbules are from different bird species. In all samples there was a marked contrast between samples ultrasonically cleaned and those that were not. Washing feathers is not very effective and even prolonged soaking did not remove a great deal of dirt when compared with ultrasonically cleaned samples. Ultrasonic activity made an immediate difference (figs. 5 & 6).

#### 4.2 Cleaning - Fibres

When viewed at high magnification two of the three flax samples were extremely dirty and in some cases fibres were actually glued together with dirt deposits. Compared to these samples the other flax sample and the wool sample were only moderately dirty with small dirt particles scattered over and between fibres. The cotton was the least soiled of the fibre samples.

The most obvious effect of the washing system was the lightening of the flax samples from dull grey/brown and grey/yellow colours to a bright, very light brown colour. This cleaning is the result of ultrasonic activity. Cleaning by prolonged soaking and manual manipulation of flax cloaks will effect some lightening of colour and minimise old stains and water-marks but nowhere to the degree ultrasonic activity will achieve (figs. 7 & 8).

The wool and cotton samples also illustrated the efficiency of ultrasonic activity in removing dirt from their surfaces.

#### 4.3 Detergent Retention

No evidence of detergent residue was found on any of the samples. The test samples were rinsed in 3 separate baths of tap water and dried in the ambient air temperature.

No attempt was made to ultrasonically rinse the samples, partly because we wanted to limit the amount of ultrasonic cavitation the sample had to experience and partly because they looked detergent-free under SEM examination, meaning such rinsing seemed unnecessary. Tap water was used as when we have washed cloaks in the past at Auckland Museum we have had to use tap water for all but the last of the rinses. This is because of the large volume of water required to rinse a cloak and consequently our limited distilled water supply is kept for the final rinsing.

#### 4.4 Cleaning Time

The earlier cleaning research had established that 2 minutes ultrasonic cavitation was adequate for cleaning feathers. The various soaking periods before introducing ultrasonic activity did, for half the feather sample, lead to cleaner feathers (figs. 9 & 10). However the bulk of the dirt was removed from the samples by simply subjecting them to ultrasonic cleaning. The same characteristics were observed in the fibre samples. Ultrasonic cleaning immediately removed most dirt. However two flax samples and the wool sample became cleaner when immersed for 45 minutes prior to undergoing ultrasonic cleaning.

#### 4.5 Effect on Colour

The possibility of a change in reflective values of structural colours in feathers as a result of ultrasonic cleaning is discussed in the earlier Auckland Museum research<sup>1</sup>. No changes of colour were observed with any blue and green coloured feathers.

#### 4.6 Effect on Shape and Structure

At low magnification there was no alteration of feather shape. No barbules were unhooking and no matting occurred. At high magnification 9 of the 11 samples were undamaged either by ultrasonic cavitation or by the dual effects of prolonged soaking with its possibilities of softening and swelling the keratin followed by ultrasonic activity. Two samples were damaged by the washing method. Peacock feathers showed a substantial loss of barbules in all samples ultrasonically cleaned. No losses showed in samples which had only been immersed but not ultrasonically cleaned. Emu feathers with their sometimes filagree-like barbule structure were damaged by ultrasonic action after being soaked for 45 minutes or longer (fig.11).

Looking at the fibres no damage in terms of fracturing, breakage or surface disruption was visible. The twist of each of the fibre strands kept its configuration and immersion for various periods in the water and detergent solution left no permanent change in fibre dimensions upon drying. The evaluation was restricted to visual indicators. Tensile strength tests on flax fibres have been carried out in the past and showed that although strength diminished by half when the fibres were wet they regained their strength upon drying.



## 5. DISCUSSION

Ultrasonic cleaning appears on the strength of present research to be very efficient and non-destructive to 9 of the 11 feather species identified on Auckland Museum feather cloaks. It is also equally efficient in cleaning discoloured and dirty fibres used in the same cloak collection.

In the course of this research we came across many aspects of textile and feather conservation which although not directly concerned with the present research helped crystalize some thoughts regarding the care of cloaks. One such piece of research were some experiments carried out at the Texas Memorial Museum on the efficiency of cleaning feathers with a vacuum cleaner. Here results reinforce the need to find an alternative to standard cleaning techniques for feathers and (by our own extension) fibres, for this work showed that vacuum cleaning is not very efficient in removing dust from feathers<sup>6</sup>.

Collating this information with this present work some generalisations can be made:

1. Vacuum cleaning is superficial.
2. Standard wet cleaning is good for superficial cleaning of all feathers and most fibres tested.
3. No cloaks which have black coloured flax fibres in them can be washed.
4. Immersion for 45-90 minutes followed by 2 minutes ultrasonic cleaning appears excellent for specified feathers and fibres.

With these results we then looked at the practicalities of introducing ultrasonic cavitation into a bath large enough to hold a cloak. We considered hand-held probes and transducers which could be either mounted at the side or bottom of the washing tank.

The probes have been used on cloaks in Denmark and on archaeological leather and textiles. Inquiries into the usefulness of ultrasonic probes in the context of cloak cleaning revealed a drawback in that they radiate only a very small ultrasonic environment. To ultrasonically clean a cloak would require an extended soaking time in order to cover its surface area with the probe.

We were also concerned about the possibility of the energy output of the probes damaging textiles and feathers. For instance, the agents for the Branson Sonifier cell disruptor used by E. van Dienst to ultrasonically clean ancient wet leather<sup>8</sup> felt that this type of equipment would be too powerful to use on cloaks. Cell disruptors, as the name implies, are designed to create a highly concentrated and intense ultrasonic environment rather than a more gentle and pervasive situation as required for our purposes.

A more suitable system of introducing ultrasonic activity into the washing solution is that of flat movable transducers. These can be immersed in the bath either by hanging them from the side of the tank or by placing them under the cloak and moving them every two minutes.

A bottom sited system suggested by Sonicator seemed the most suitable. With this system sets of transducers packaged in stainless steel units can be placed under the cloak and its support at the bottom of the tank. The unit is connected by cable to a generator and can be moved around underneath the cloak as each 2 minute ultrasonic cleaning cycle is completed. The immersible we have in mind operates at the same frequency as the Sonicator SC200 used in the tests and radiates ultrasonic waves over a 15 x 46 cm area. Rapidity of cleaning depends on how many immersibles are operating. Looking at the dimensions of the cloaks in the Auckland Museum collection most cloaks could be ultrasonically cleaned in about 30 minutes if two immersible units are utilized.

Having said this we feel that more work could be done on identifying the most suitable ultrasonic transducer for cleaning ethnographic material.

## 6. CONCLUSION

The ultrasonic cleaning tests described here show that these fibres and feathers can withstand immersion in aqueous solutions for at least 90 minutes followed by 2 minutes of ultrasonic cleaning with no discernible harm to them. The exceptions are the black coloured flax fibre, peacock and emu feathers.

The tests also showed the superficial nature of conventional cloak washing treatments. Surface dust will be removed by these methods but more resistant dirt deposits which are long term threats to old textiles are on the evidence presented here unaffected by such washing.

Looking at the cleaning tests the point that must be emphasized is that one cannot yet draw generalizations from the results we have obtained.



Fig.7 Flax fibre after being immersed in the washing solution for 45 minutes, approx. 850X mag.



Fig.8 Flax fibre after being immersed in the washing solution for 45 minutes followed by 2 minutes ultrasonic cleaning, approx. 850X mag.

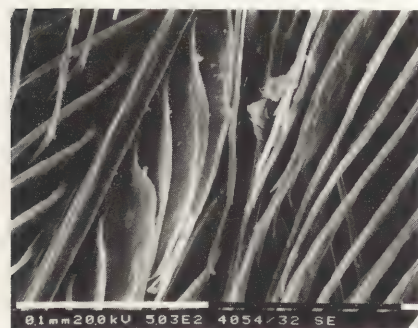


Fig.9 A kaka feather subjected to 2 minutes ultrasonic action only, approx. 500X mag.

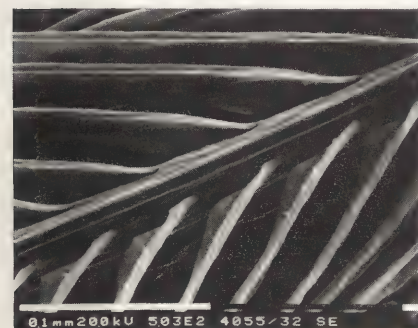


Fig.10 A kaka feather immersed for 90 minutes followed by 2 minutes ultrasonic action, approx. 500X mag.



Fig.11 An emu feather breaking up after 90 minutes immersion in the washing solution followed by 2 minutes ultrasonic cleaning, 500X mag.

The adverse results we have experienced in cleaning feathers from the New Guinea pigeon, peacock, and emu illustrate this well. These feathers have no common structural characteristics that we could identify and each suffered degradation from the cleaning technique that is specific to itself. Other feathers will no doubt react similarly.

Input from colleagues on this project has been very gratifying. Included in the criticism and advice have been some suggestions on ways of tightening up on the parameters of the research. One suggestion was that we should be more exact in establishing just what the dirt is that we are trying to remove from cloaks. As practical conservators we feel this is impossible as the cloaks have had a long and often rugged life both in the Maori community and later in the Museum. They may have been laid on the ground and sat upon, stored in a folded state in an attic for decades, pinned on display in open, brightly lit conditions for half a century: the possibilities are endless. Another suggestion has been to make a comparison between sound and degraded feathers of the same species. In our work situation we feel we cannot justify the time to carry out tests on sound feathers and feel the present range of comparisons is adequate in identifying the suitability of ultrasonic cleaning. First and foremost we are hands-on conservators attempting to identify an efficient method of cleaning fragile material which, on growing evidence, has not been particularly well cleaned in the past, despite the best intentions of all of us in the field of ethnographic conservation.

#### REFERENCES

1. BARTON, G. & WEIK, S., Ultrasonic cleaning of ethnographic featherwork in aqueous solutions. *Studies in Conservation*, Vol.31, no.3 (1986).
2. BARTON, G., Ultrasonic cleaning tests in aqueous solutions on Maori cloak materials. Auckland Museum 1986.
3. MEAD, S.M., *Traditional Maori Clothing*. Reed, N.Z. 1969.
4. HOFENK-DE GRAAFF, J.H. The constitution of detergents in connection with the cleaning of ancient textiles. *Studies in Conservation*, Vol.13, no.3 (1968).
5. BARTON, G., Care of cloaks at Auckland Museum. *Tu Tangata* 25 (1985).
6. PETERSON, K.S. & SOMMER-LARSEN, A., Cleaning of early feather garments from South America and Hawaii. ICOM Conservation Committee 7th Triennial Conf. Preprints (1984).
7. WOLF-GREEN, S. & STORCH, P.S., An evaluation of feather cleaning techniques. Symposium 86. The care and preservation of ethnological materials. Canadian Conservation Institute, 1986, unpublished.
8. VAN DIENST, E., Some remarks on the conservation of wet archaeological leather. *Studies in Conservation*, Vol.30, no.2 (1985).



## SUMMARY

Rare instances of beads degenerating to an amorphous waxy mass were observed. This proved to be a water soluble soap produced by the interaction of decaying beads with oily material from the leather substrate.

DETERIORATION OF GLASS TRADE BEADS IN CONTACT WITH SKIN AND LEATHER  
OR  
GLASS BEADS IN SOAPY BUBBLE\*

Julia Fenn  
Conservator of Ethnology and Folk Art  
Royal Ontario Museum  
Conservation Department  
100 Queen's Park, Toronto, Ontario M5S 2C6 Canada

Deteriorating European-made glass beads on Ethnographic artefacts is a recognized problem. Recent articles by Loughheed and Shaw,<sup>2</sup> and Howatt-Krahn<sup>3</sup> have described the causes, the early diagnosis, and the symptoms of inherent instability in glass beads, as well as some of the effects on contact materials, and the general care of beadwork in general.

At the Royal Ontario Museum we have a visually appalling variation on the usual type of glass bead decay. Unstable glass beads on a few pieces of beadwork attached to skin or leather are being converted into soap. The apparent cause, which has been confirmed by recent analysis at the Canadian Conservation Institute,<sup>4</sup> is that hygroscopic alkaline salts have leached out from the very poorly stabilized potash glass and reacted with fatty material in the leather to form a soap; a soft potassium soap with a pH between 9 and 10. It was not clear whether the alkaline salts were derived entirely from the breakdown of particularly unstable groups of beads, or whether the glass deterioration itself was initiated by residues of alkaline lubricants, such as saddle soap in the leather. The presence of this soap in continuous direct contact with the rest of the unstable glass ensures its progressive dissolution until no vestige of the silica network remains. The result is a soft swollen, sticky amorphous sludge; a very unappealing substitute for the original beads.

I was first made aware of this type of deterioration four years ago when June Hosford from the South African Museum of Natural History sent me some photographs of a modern Ndebele native-tanned skin apron made during the 1960's, which was suffering from "waxy deterioration" of the Czechoslovakian orange glass beads. Simple tests established that the beads were not resin or resin-coated and that the "wax" had a high pH, was water soluble, but not readily soluble in organic solvents such as ethanol, hexane, acetone and toluene. After showing the photographs to our Ethnology Department they found a worse example from our own collections. It was an Assiniboine woman's belt of vegetable tanned leather made in the early 1900's and collected soon afterwards. The glass beads were thought to be from Italy.

At first I was not unduly concerned because the problem seemed to be an interesting but rare phenomenon, not likely to be a major threat to Ethnographic beadwork collections. This belief in its rarity was re-inforced by the fact that the Canadian Conservation Institute's bead project did not uncover any more examples.

Since then I have changed my mind. Only recently I discovered a few more examples in parts of our collection which had already been examined, which may mean that the early symptoms are too subtle to be easily recognisable. Considering that only three factors seem to be necessary to initiate this type of deterioration, it may prove to be a more common occurrence than it seems at present:

1. A very high pH. This could be derived from a few poorly stabilized beads, or from cleaning agents trapped in the beadwork after surface cleaning. When beads are attached to skin, extra care is taken to avoid aqueous methods of cleaning. Dry sodium bicarbonate is occasionally used, or organic solvents sometimes in combination with spirit soaps such as Vulpex B30 - a highly alkaline potassium oleate soap. Even with very careful swabbing, spirit soap solutions can be drawn into the beadwork by capillary action.

\*'Soapy Bubble' is 'trouble' in Cockney

2 Loughheed & Shaw, "The deterioration of Glass Beads on Ethnographic Objects," *The Bead Forum*, No. 7, 1985, pp. 10-12;

Loughheed, "The deterioration of Glass Beads on Ethnographic Objects," *Proceedings of Symposium '86 - The Care and Preservation of Ethnological Material*, Ottawa, September 1986, forthcoming.

3 Howatt-Krahn, "Beadwork," *American Indian Art Magazine*, Autumn 1986, pp. 24-29.

4 Sirois & Williams, *C.C.I. Analytical Report*, ARS No. 2396.

2. Moisture. The hygroscopic properties of skin or the alkaline salts from the beads might provide a sufficiently moist micro-climate, especially if they are kept at the high RH levels currently considered suitable for the storage of Ethnographic skin artifacts. Water trapped inside the beads from wet cleaning methods is another possible source.

3. Fatty material in the skin. Where a potentially unstable batch of beads is sewn on a skin material, the application of traditional leather dressings may be all that is needed to initiate soapy disintegration. Raphael and McCrady<sup>5</sup> have already produced a convincing argument against the indiscriminate use of such dressings, this may be one more reason for exercising restraint. As yet it is not clear whether all oily dressings could damage such beads to some degree, or whether it is only emulsions and soap-based lubricants which pose the greatest threat. Not all soapy material can be attributed to museum treatments. Laundry soaps have been used in native tanning and European vegetable tanned leather was sometimes "filled" with soap to improve the handle.

These are not an unlikely combination of circumstances. Given the possibilities, it will be surprising if a few more examples do not begin to appear, but I must stress that it is all highly speculative at this stage. I have identified only five artifacts with this type of deterioration, whereas there are many which show the more usual cracking deterioration or powdery salt efflorescence, and have not reacted with the substrate.

Soapy degeneration is not only a very unsightly form of deterioration, it causes progressive irreversible destruction of the artifact. Unlike crizzled beads which often crack and fall off the artifact, soaping beads remain on the artifact and ooze nastily into the surrounding beadwork and the substrate. In this form it rots the leather and can create spreading "tidemark" stains. Even stable glass beads held in continual contact with this moist alkaline material, will eventually deteriorate in the same manner. The soft soap is able to wick along the threads for about 2-3 cm. so that even beads which are not directly adjacent begin to deteriorate from the inside out. Under these circumstances the deterioration of other colour elements at some distance from the worst areas may be quite far advanced before the damage is detected. Judging solely from the very few samples I have, the process seems to start slowly, then becomes more rapid. The Assineboine belt has been kept in Ethnology storage, where the RH averaged about 47%, and is visibly degenerating. Four years ago there were still a few orange beads left as witness to their original appearance, while the adjacent rows of translucent yellow beads had just begun to break down. Now the yellow beads are barely distinguishable, and three other colour elements show advanced interior dissolution.

Since the damage is irreversible I am anxious to find ways of stopping the spread of this type of deterioration once it has been recognized. Reducing the humidity should certainly slow down the attack, but it is doubtful whether, if once hygroscopic salts are present, the RH could be lowered sufficiently to prevent any further damage. Excessive drying could also damage other components of the artefact, for example the skin itself, or sinew threads, which are notoriously prone to snap if they lose too much moisture. Nevertheless I am keeping a control group of partly saponified beads at the RH levels recommended by Loughheed<sup>6</sup> (RH 35-40%) for comparative purposes.

The removal or replacement of the decaying beads could be another solution, but for ethical reasons it would usually be considered unacceptable. In one case I have been able to insert thin sheets of Mylar<sup>TM</sup> (polyethylene terephthalate) to act as an inert barrier between the beads and the skin. However in most cases this would be impossible without cutting the original threads attaching the beads to the substrate. It is also very difficult to insert the flexible Mylar smoothly and inconspicuously without putting stress on the sticky strands of beads. Thicker grades of Mylar which are easier to insert have unacceptably sharp edges.

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<sup>5</sup>Raphael & McCrady, "To Dress or Not to Dress,"  
Leather Conservation News, No. 10, December 1983

<sup>6</sup>Loughheed, op. cit.



At the moment I am experimenting to see whether it is possible to reduce the wicking properties of the threads in situ without making them too stiff. Perhaps the absorbant properties of threads should become a more important consideration when selecting threads for repairing beadwork. Cotton, often used because of its other desirable properties, transmits moisture and oils very readily. It would also be interesting to know how the common practice of waxing threads affects the transmission of soaps and alkalis.

As a last resort I am also experimenting with methods of removing surplus oils or soaps from the skin and reducing the pH to a more normal range. If feasible this might be a suitable treatment for cases where the original nature of the skin preparation has been irretrievably altered by the addition of unsuitable preservatives in accordance with the ideas of an alien culture. But, it would be a highly dubious procedure to remove these materials if they have been introduced as part of the indigenous technology.

It would be premature to make any definite recommendations at this stage, because there are still so few examples, and these have been under observation for such a short time. The existing ones are undergoing further analysis and I am attempting to reproduce the degeneration under laboratory conditions. At the same time other museums are being asked to check their collections in the hope that a larger number of cases will help to define the key agents of soapy degradation more closely.

#### BIBLIOGRAPHY

1. Howatt-Krahn, A., "Beadwork," American Indian Art Magazine, Autumn 1986, pp. 24-29.
2. Loughheed, S., "The deterioration of Glass beads on Ethnographic Objects," Proceedings of Symposium '86 - The Care and Preservation of Ethnological Material, Ottawa, September 1986, forthcoming.
3. Loughheed, S., & Shaw, J. "The deterioration of Glass Beads on Ethnographic Objects," The Bead Forum, No. 7, 1985, pp. 10-12.
4. Raphael, T. & McCrady, E., "To Dress or Not to Dress," Leather Conservation News. No. 10, December 1983.
5. Sirois, J., & Williams, S., C.C.I. Analytical Report, ARS No. 2396.





## SUMMARY

The literature survey on the effects of ethylene oxide on artifact material shows explicitly that there are potential changes in materials of artifacts on fumigation with ethylene oxide, e.g. chemical solubility, pH, adsorptive ability and strength characteristics, as well as introducing humectants and products of ethylene oxide.

Ethylene oxide, and its products ethylene glycol, which may form in artifact materials, are hazardous to man. They are mutagenic, carcinogenic and toxic, and difficult to monitor.

Freezing of artifacts under specific conditions and using specific procedures has been recommended as an alternative.

The literature survey on the effects of freezing on materials that would be found in artifacts shows that there are potential water hazards which can easily be prevented. Bound water in dry artifact material and water in damp materials in capillaries less than 30 $\mu$  will not form ice crystals at -20°C. Condensation caused by reduced holding capacity of air or warm air cooling adjacent to cold objects can be prevented. Freezing should not be used for non-adsorptive materials. Physical and dimensional changes are minimal at the recommended -20°C.

Essential procedures for freezing artifacts are listed.

## THE EFFECT ON ARTIFACT MATERIALS OF THE FUMIGANT ETHYLENE OXIDE AND FREEZING USED IN INSECT CONTROL

Mary-Lou Florian  
Conservation Scientist  
British Columbia Provincial Museum

1. Introduction

The purpose of this paper is to bring together information on the effects on materials of artifacts, of the fumigant ethylene oxide when used to eradicate insects and freezing as an alternative to the use of the toxic chemical for insect eradication.

2. The effects of ethylene oxide on artifact materials2.1 Ethylene oxide reactivity

Ethylene oxide, the simplest epoxy compound, is a very reactive chemical. It owes its high reactivity to the ease of opening the highly strained three-membered ring and readiness to combine with compounds which contain a replaceable hydrogen atom. This process is called alkylation which is usually defined as the replacement of an available hydrogen atom with a chemical group such as the amino, carboxyl, hydroxyl group, etc. with a hydroxyl ethyl radical (which is the alkyl group). The biocidal activity of ethylene oxide is due to alkylation. The great reactivity of ethylene oxide makes it the starting material for many industrial chemicals (1,2,3).

Ethylene oxide reacts readily with water to form ethylene glycol. The moisture in dry museum artifacts is in the form of bound water not available for reactions. But artifacts which have free water such as waterlogged artifacts or wet artifacts with humectants, would be sites for ethylene glycol formation. Ethylene glycol is a humectant itself and is also a solvent for paint, plastics (4) and gelatine (5).

Ethylene oxide readily reacts with phenols. In museum collections phenols are present as vegetable tannins in herbarium specimens and plant parts used in fabrication of material culture and in vegetable tanned leather. Selective methylation of tannins alters them chemically which could reduce their natural antioxidant ability (6).

Ethylene oxide reacts with metallic halides to form the extremely toxic haloalcohol and a metallic hydroxide. This specific reaction is used to monitor penetration of ethylene oxide during the fumigation process (7). The common halides are chlorine, bromine, iodine and fluorine.

Halides are found in many artifacts, i.e. salt contaminants, mordant for dyes, corrosion product, polyvinylchloride, hypochlorite bleach, chlorinated pesticides (pentachlorophenol & D.D.T.). It is not known if the bromide left after methyl bromide fumigation will enter into this reaction. Another aspect of this reaction is that it is strongly exothermal.

Ethylene chlorohydrin is a liquid which is less volatile than water and can form solutions with many materials and thus dissipates slowly. It is more toxic than ethylene oxide and a human hazard because it is readily adsorbed through the skin. It has been reported to occur in polyvinylchloride medical devices and saline pharmaceuticals fumigated with ethylene oxide (8). Because of the presence of this toxic chemical, the Environmental Protection Act (8,9) in USA requires that dissipation curves of the ethylene chlorohydrin must be established to determine when it is safe to use the above materials. There is no way of determining this without destructive analysis.

Ethylene oxide reacts with the alcoholic hydroxyl group in natural and artificial cellulose to form hydroxyethyl-cellulose. In the paper and textile industry (10,11) ethylene oxide is used to improve the wet strength of paper and to form protective colloids for sizing paper and textiles. Cellulose is present in artifact materials made from plant parts or wood (textiles, paper basketry) and also in herbarium specimens.

Ethylene oxide readily alkylates proteins. The effects of alkylation on proteins are changes in the isoelectric point 1-3 pH units, solubility, and electrophoretic mobility (12).

A striking increase in adsorption of water of intact collagen occurs after alkylation (13) and the treatment of silk fibroin with mono- and multi-functional epoxides (14) increases moisture regain and increase flexibility and crease resistant properties.

Merino wool alkylated with an alkyl halide, adsorbed more water at high humidities than unmodified wool (15).

There are many other chemicals reported in the literature with which ethylene oxide can react: vitamins (16,17); amino acids (18); fatty alcohols, organic and inorganic acids, hydrogen sulfide, alcohols, amines (1); and fatty acids (19). These chemicals could be found in some materials of artifacts.

## 2.2 Effects on commercial materials

For the museum professional, an important question arises, do these reactions occur during standard fumigation of dry artifact materials, and are the reaction products retained? One may argue that the chemical and physical parameters (concentration, temperature, catalyst, etc.) which are required for the industrial reactions are certainly not met on simple vacuum fumigation at ambient temperatures using the standard commercial mixture of approximately 10% ethylene oxide to 90% inert gas (generally freon or carbon dioxide). But in the literature there are many reports of the presence of ethylene oxide, ethylene glycol and ethylene chlorohydrin in dry materials, spices, pharmaceuticals, plastics and physical changes in dry materials after commercial fumigation.

In whole and ground spice mixtures, 1000 ppm ethylene chlorohydrin was present after commercial fumigation and was shown to be sufficiently involatile and chemically unreactive to be persistent under food processing (20). The formation of high concentrations of ethylene chlorohydrin is possible because the carbon dioxide in the gas mixture acts as a buffer to maintain a pH which favors ethylene chlorohydrin formation (20). In the 1965 paper the authors stated "it would seem that a case exists for proposing that fumigation of food stuffs with these agents should be discontinued forthwith." (20)

More recently (1981) in Sweden, high levels (70 - 3730 mg/kg) of ethylene chlorohydrin were reported (21) in imported spices intended for industrial manufacturing of foods.

The formation and retention of ethylene glycol and ethylene chlorohydrin in the following various materials was shown to occur after fumigation i.e. for ethylene glycol: 4270 ppm was retained after 70 days in natural sponge; 2650 ppm after 30 days in powdered starch; and 260-520 ppm after 180 days in cotton wool. For ethylene chlorohydrin: 12 ppm was present in gelatine granules 180 days after fumigation; and 400 ppm after 30 days in powdered starch (22).

The presence and persistence of ethylene oxide in plastics after fumigation has been reported (23,24). The sorption of ethylene oxide in plastics such as polyethylene (polyolefins) is considered to be a solubilization process and not a simple physical entrapment of the gas, thus, it is not readily desorbed (24). The amount adsorbed and the rate of desorption depends on the plastic.

In 1969 (24) because of the toxicological problem in using plastic medical devices, tubing, etc. which have been fumigated by ethylene oxide (the standard procedure for sterilizing of heat labile materials) it was stated "the foregoing toxicities should serve notice to those charged with the responsibility of gas sterilization and that some further analytical toxicological studies are needed or sterilant-plastic interactions studies before ethylene oxide is accepted as a completely safe means of sterilization." Today in 1987, we still have not faced the problem squarely.

In the museum world, polyethylene bags and wrappings are commonly used to protect artifacts. During fumigation the same reactions as is described for devices will occur with this plastic, presenting the same hazard of retention of ethylene oxide.

## 2.3 Effects of ethylene oxide fumigation on materials of artifacts

An increase in strength of papers treated with ethylene oxide in library artifact material has been reported (7). These changes can be explained by the alkylation of cellulose and formation of hydroxyethyl cellulose which increases strength of cellulose.

The retention of ethylene oxide in leather (23) and shoes (25) is well documented. Fumigated parchment showed no strength changes but was more sensitive to microbial attack (26). This could be explained by the increase in adsorptive ability of collagen (13) or by the formation of ethylene glycol which would act as a humectant and increase the moisture content of the parchment.

The viscosity, adhesion and color of inorganic and organic pigments and pigment binding materials used on illuminated parchments were tested after ethylene oxide fumigation. The only changes were the loss of adhesion of casein and egg white. These results could well be explained by the alkylation of the protein and changes in solubility (12). It was stated (in 1978) that because of potential changes of artifact materials, "Ethylene oxide treatment should not be employed indiscriminately, but only in those cases in which microbiological attack is present and represents a real danger to the conservation of the piece of art." (27)

Analyses of gut used for Inuit garments showed that the isoelectric point changes after ethylene oxide fumigation (28), also verifying the alkylation reaction.



An important aspect to altering materials of artifacts is the loss of potential research information. Amino acids may be changed and no longer give valid reactions for racemization dating. Protein may be altered and cannot be used for species identification (29) using such techniques as isoelectric focussing (28,30,31) which depend on isoelectric mobility. Chemicals in herbarium specimens may be altered and may no longer be useable for chemotaxonomy.

Ethylene oxide, ethylene chlorohydrin and even ethylene glycol are hazardous chemicals for man (8). There are mutagenic, carcinogenics and toxic. The EPA (9) in the past few years have lowered the limits of acceptable amounts of environmental ethylene oxide in the work area of fumigation to such a point that many fumigation chambers are illegal to use and also monitoring devices used are not sensitive enough to detect such low levels. Also we have no way of monitoring ethylene chlorohydrin in artifacts, thus the elimination of the health hazards seem insurmountable.

Thus because of the tremendous health hazards and the alterations of materials it seems logical to be looking to a non-toxic alternative method of insect eradication. Freezing of artifacts under specific conditions and using specific procedures has been recommended as an alternative (32,33).

### 3. The effects of freezing used to eradicate insects on artifact materials

#### 3.1 Water relationships

##### 3.1.1 Ice does not form in dry artifact material

In dry artifact material at equilibrium moisture content with the museum environment, the moisture in materials will be bound moisture which is not available for reactions or ice formation. In the freezing of dried beef muscle containing 20% moisture content (MC) and gelatine gel with 35% MC there is no ice formation. Water in the gelatine of motion picture films, dried at 50% RH, is unfreezeable (34). Bales of wool at  $-11^{\circ}\text{C}$  and wool cooled to  $-50^{\circ}\text{C}$  and  $-70^{\circ}\text{C}$  showed no phase change which would indicate bound water freezing (35).

During the freezing process, the associated air will increase in RH and the artifact material will increase in moisture content. If excessive the water may be free water associated with pores or capillaries of the material, and this water, still, will not be available for ice formation. In fresh collagen samples with water 45%–60% the water did not freeze at temperatures as low as  $-50^{\circ}\text{C}$  (36). The reason for this is related to the fact that water in fine capillaries below 30  $\mu$  in diameter does not freeze (37). The water in the capillaries is physically altered, it is similar to bound water in that it does not have solvent power and does not form ice, also it has higher viscosity and thermal expansion, lower water vapour and is more stable than free water.

Ice will not form in dry artifact materials subjected to  $-20^{\circ}\text{C}$ , the recommended temperature for insect eradication (33). When waterlogged material is frozen, ice crystals will form.

##### 3.1.2 Freezing of water vapour

Water vapour freezes in dust free air in the Wilson chamber at  $-41.2^{\circ}\text{C}$ , in outdoor air at  $-32.2^{\circ}\text{C}$  and in smoke filled air at  $-27^{\circ}\text{C}$  (38). The freezing depends on nucleation particles. Thus the freezing of the water vapour in the freezer chamber or in the air in the bag with the artifact should not occur at the temperatures used for eradication of insects.

##### 3.1.3 Condensation of water

We are familiar with water condensing on cold objects placed in warm humid air. The warm air adjacent to the cold surface of the artifact is cooled, its moisture holding capacity is lowered and the excess moisture vapour condenses to form dew or water and if it freezes, frost on the surface. Rapid air circulation due to temperature differentials between the air and the cold surface is continually supplying warm air to the cold surface causing a visible build up of frost or water depending on the temperature of the surface.

On placing an air-tight polyethylene bag filled only with air of 50% RH and  $19^{\circ}\text{C}$  into the freezer, as the air cools some condensate will form on the inner surface of the bag. The explanation of this is simply that as the air cools, the holding capacity of the air decreases and when 100% RH is reached the excess water condenses on the non-adsorbent plastic bag. Condensation will also occur on non-adsorbant materials placed in the bag such as glass, metal, plastics, etc.

If an artifact made of adsorbent material is placed in the bag under the same conditions, condensation may not occur if the artifact material is able to adsorb all the excess water and the rate of cooling will allow total adsorption of the excess water. Reducing the amount of air by vacuum packing will reduce the amount of excess water dramatically, thus preventing condensation. This can also be accomplished by introducing buffering adsorbent materials (39,40) or pretreated silica gel (41,42).

When a bagged artifact is removed from the freezer condensate will form on the outer surface of the bag until ambient temperatures are reached. The small amount of air in the bag will be warmed and increase its moisture holding capacity and will not cause condensation.

#### 3.1.4 Regain ability of artifact materials

During cooling the moisture content of artifact materials will increase due to decrease in temperature (43) and increase in RH. The amount of moisture adsorbed will depend in part on the regain ability of the material.

Retain ability of materials is variable and may be due to inherent characteristics, treatment, deterioration, and sorption history of the material as well as environmental parameters.

Inherent characteristics are: Molecular structure changes during sorption (44); available hydrogen bonding sites, protein denaturation, degree of polymer crystallinity or amorphous regions and available surface area (45); and solubility (46). Treatments such as tannage, alkylation, acetylation, deamination, impregnation with humectants as well as shrinkage and photochemical degradation (47) will alter moisture regain. The sorption history of materials is a result of successive adsorption and desorption cycles which may result in loss of hysteresis and reduced moisture regain (45).

The parameters of the environment influence sorption. The equilibrium moisture content (EMC) increases and the rate of sorption decreases with decrease in temperature (44). The vapor pressure of the water in materials, which governs the diffusion gradient, decreases as sorption occurs and is dependent on temperature, moisture content, pH, and sorption history (35).

If an artifact made of adsorbent material is placed in a polyethylene bag, and the excess air is removed or it is vacuum packed, condensation will not occur on the object nor ice form in the material, if the regain ability of the material is able to adsorb the excess water from the cooling air and the rate of sorption is rapid enough. The obvious question is how do we know the regain of the material?

In the literature regains of many materials are reported (33,41,48,49,50, 51,52,53) e.g. nylon has 3.5% EMC at 50% RH and 8% EMC at 100% RH adsorbing 4.5% or 4.5 grams of water in 100 grams, methylated wool changing from 9% EMC to 46% EMC can adsorb 35 grams of water in 100 grams, and collagen from 15% to 55% EMC can adsorb 40 grams of water in 100 grams. This shows the range from relatively non-adsorbent nylon to readily adsorbent collagen.

The amount of water adsorbed is significant when you compare it to the available water in the polyethylene freezer bag. If the bag contained a square meter of air at 50% RH cooling from room temperature to 0°C it will have an excess of 7 grams of water. If the nylon was placed with this cubic meter of air, condensation would occur, but the other materials would readily adsorb the excess water. It would be extreme to place 100 grams of nylon in a cubic meter container, if the air volume was reduced by half condensation would not occur. The logical approach is to eliminate as much air as possible or vacuum pack and do not freeze non-adsorbent materials.

The rate of adsorption occurs rapidly, in a few minutes (49,53) at the onset of increase in RH but is dependent on packing.

### 3.2 Physical effects of freezing temperatures

#### 3.2.1 Introduction

It is important to note that many artifacts made from insect vulnerable organic materials have gone through freeze/thaw cycles during usage. The materials of the Canadian Arctic Inuit (54,55): driftwood; soap-stone; seals' blood glue; antler; walrus; tusk; bones; untanned animal skins; and sinew, during usage have gone through many freeze thaw cycles without appreciable damage and composite artifacts such as: the bone or antler laminated bow; arrows made of wood and feathers with copper, bone or iron heads and sleds of wood, bone and rawhide, all survived the freezing temperatures of the arctic during usage.

It is possible that all material culture of aboriginal people from temperate and arctic regions has been frozen without damage. It is another story with artifacts from the tropics and from controlled temperature dwellings which have not been exposed to freezing temperatures.

Whether or not this exposure to freezing has enhanced degradation is another question. But it is our ethical responsibility as conservators to determine to the best of our ability if additional freezing treatments are damaging to artifacts that are now in the museum environment.

Information about the physical changes of materials at low temperatures is found in the literature on aeronautical research and materials research for the arctic, refrigeration, cryobiology, and wood technology.



### 3.2.2 Wood

Minimal dimensional changes in wood do occur due to lowering the temperature (56), for example wood at a constant 12.8% EMC (similar to EMC in the museum environment) subjected to  $-20^{\circ}\text{C}$  shows shrinkage of  $-0.3\%$  tangentially and  $-0.1\%$  radially. Similar longitudinal changes may also occur (57). The dimensional changes follow the temperature changes immediately and on reheating the wood reswelling follows the increase in temperature. This shrinkage is due to thermal contraction.

During the freezing process used for eradication of insects the EMC is not constant, the small thermal contraction in dry wood would be overcome by the swelling caused by increase in moisture content (50).

Physical strength characteristics of wood, i.e. modulus of elasticity, maximum crushing strength, increase with decrease in temperature (58,59,59). Also the higher the moisture content the greater is the strength-increasing effect of the low temperatures. Embrittlement of the wood occurs at temperatures much less than  $-20^{\circ}\text{C}$  (59).

### 3.2.3 Adhesives

In reference to adhesives, extrapolation from the literature shows that at  $-20^{\circ}\text{C}$ : urethane based adhesives used for light weight air-transportable arctic shelters and cryogenic containers (61); phenol, melamine, resorcinol based adhesives used in glulam plywood (laminated wood) (57); urea-formaldehyde and phenol formaldehyde glue joints at the different moisture contents of 8, 12, and 18% MC (58) showed no change or an increase in shear strength. Casein joints (58) showed a decrease of approximately 10% in shear strength, with increase of moisture content.

### 3.2.4 Textiles, motion picture film, polymers

The behaviour of textiles under low temperatures have been investigated for garments for use in the arctic and outer space, this literature has not been reviewed. Fibers tested (62) at temperatures from  $57^{\circ}\text{C}$  -  $177^{\circ}\text{C}$  showed that the fibers are strongest at the lower temperature and decrease in strength as the temperature increases.

The effects of freeze/thaw cycling on motion picture films have been investigated (34). Empirical results showed that film stored in heat-sealed foil bags equilibrated to 50% RH, that after annual inspection no adverse effects on the image stability was observed after 10-15 years. Experiments testing changes in wedge brittleness, mushiness, and wet and dry adhesive tests, showed no adverse effects on films placed in heat-sealed foil bags at 25-35% RH, which were then placed in a film can, taped, stored in a freezer at  $-12$  -  $15^{\circ}\text{C}$  over a period of 6 months of daily cycling of thawing for 4 hours.

Comparing strength differences of a group of polymers at low temperatures, polyethylene shows good flexibility but polyvinyl chloride and crosslinked epoxy resin systems are brittle (63).

The cause of the brittleness in polymers at low temperatures is described (64) - "the chains of amorphous polymers are entangled. At low temperatures most degrees of freedom are frozen; the chains, therefore, become stiff--and under load without normal plastic flow brittle fractures occur."

The stiffening point of most of the elastomers is below  $-20^{\circ}\text{C}$ , and the brittle point is below  $-50^{\circ}\text{C}$  (65).

Fiber composite materials used in the arctic such as glass fiber-epoxy, gets stronger and stiffer as the temperature decreases and the thermal contractions at  $-20^{\circ}\text{C}$  are only in the order of  $10^{-4}$  (55). These fiber materials are used to replace brittle-matrix materials such as cement, concrete and ice which tend to fracture easily at low temperatures.

Embrittlement due to decrease in temperature is reversible.

## 4. Summary

### 4.1 Summary of effects of ethylene oxide on artifact materials

In summary, the literature survey shows explicitly that there are potential changes in materials of artifacts on fumigation with ethylene oxide, i.e. introducing humectants, strengthening paper, changing solubilities, pH and adsorptive ability. The question arises, are these changes all deleterious? Some may be of advantage. How are we able to judge? How indeed? For example, increasing the adsorptive ability of parchment may make it more pliable but it may also make it more prone to biodeterioration, or changing the physical properties of paper may present the ethical question of permanently altering materials.

### 4.2 Summary of water relationships

In dry artifact material, the bound water will not form ice crystals. In damp materials, free water in capillaries less than 30u will not form ice crystals. Ice may form in wet materials.

The water vapour in the freezer chamber or in the air in the bag with the artifact should not freeze at the temperatures used for eradication of insects.

Condensation is the result of reduced holding capacity of air or warm air cooling adjacent to cold objects.

Condensation on artifact material is easily eliminated by reducing the amount of air by withdrawing air or vacuum packing in a sealed bag or introducing buffering adsorbant materials.

When a bagged artifact is removed from the freezer condensate will form on the outer surface of the bag until ambient temperatures are reached.

The regain ability of materials vary because of inherent characteristics, treatment, deterioration, sorption history and environmental parameters.

From this information several important requirements for a logical procedure for freezing artifacts are apparent: the artifact should be bagged in a water impermeable clear film; it is desirable to remove as much air from the bag as possible (vacuum pack if possible); pretreated silica gel could be used to lower RH of air in large bags to remove moisture that may condense at  $-20^{\circ}\text{C}$ ; and precautions should be taken not to remove artifacts from bags until they have reached ambient room temperatures, and until water that may have condensed on the outer surface of the bag has evaporated.

#### 4.3 Summary of effects of freezing on the physical characteristics of artifact material

Inorganic materials which are non-adsorbant, would rarely be treated by freezing, i.e. metals, ceramics, glass, etc. The biodegradable vulnerable group includes the adsorbant organic materials, textiles, wood, plastics, and materials of animal (horn, baleen, feathers, etc.) and plant (leaves, seeds, fibers, etc.) origin.

The most important fact to realize is that the majority of the materials in aboriginal artifacts have been frozen at some time during their usage.

Very little pertinent information was found in the literature on changes in materials due to the freezing temperatures that would be used in freezing for insect eradication.

In reference to wood, decrease in freezing temperatures causes increase in strength characteristics. Also increase in moisture content increases these strength characteristics. Swelling of wood will occur if increase of moisture content accompanies temperature decrease.

Adhesives, and wood/glue lines for arctic use also do not show significant bonding strength changes at  $-20^{\circ}\text{C}$ .

Most plastics on cooling will become brittle but not significantly at  $-20^{\circ}\text{C}$ .

#### 5. Conclusion

From the above information freezing as an alternative to toxic chemicals for insect control is recommended. To freeze artifacts special procedures are required. The following procedures have been suggested (33):

1. When using a chest freezer, infested artifacts should be bagged in airtight clear polyethylene film, and partially evacuated, the amount depending on the stability of the artifact and its tolerance to the pressure of the film against it. When using a controlled temperature and humidity freezing chamber, bagging is not necessary. Precautions should be taken when bagging infested materials, because as soon as the artifact is in the bag, insects will respond to the environmental change and try to escape, therefore seal immediately.
2. When using a chest freezer, if the artifact is large (i.e. furniture), pretreated silica gel or absorbent materials can be included with the artifact in the bag to absorb the excess water due to cooling of the air around the artifact and to maintain a relative humidity below 100%.
3. Bagged and infested materials should be kept at room temperature (above  $18^{\circ}\text{C}$ ) until placed in the freezer. In an emergency, they may be placed in a refrigerator until freezer space is available, but should not be temporarily stored in a cold basement or cold storage with temperatures above  $5^{\circ}\text{C}$ .
4. There should be adequate air circulation around the artifact to allow it to cool at at least  $0^{\circ}\text{C}$  in four hours.
5. Thermo-couples should be used to record the time/temperature parameters of the freezing procedure, i.e. the rate of cooling and thawing, and the time at the minimum temperature of the artifact.



6. The minimum temperature has been established at  $-20^{\circ}\text{C}$ .
7. The time span at the minimum temperature has been established at 40 hours.
8. A slow rate of thawing is desirable, i.e. when the rate of increase of temperature cannot be controlled, place materials directly from the freezer into a refrigerator or cold storage and leave there until thawed; or slowly increase the temperature of the freezer up to  $0^{\circ}\text{C}$  over a period of 8 hours (arbitrary).
9. It is desirable to immediately repeat the freeze-thaw cycle.
10. If possible, leave artifacts in the polyethylene bag for storage. Do not remove the bag until the artifact has reached room temperature and there is no condensed water on the outside of the bag. Insect remains should be removed if present.
11. A record of all the above procedures should be made and included with the condition report for the artifact. The record should include: identification, stages, and activity of the insects; packaging materials and method; time required to bring materials to  $0^{\circ}\text{C}$  and to minimum temperature; time materials were held at minimum temperature; time required to bring materials to room temperature; any physical changes observed; and the success of the procedure.

#### References

1. Anon. "Materials and Technology". Longmans. Harlow, England. Vol 4 (1968-75): pp. 336-348.
2. Anon. Chemical Technology. Barnes & Nobel, N.Y. Vol. 8 (1969).
3. Morrison, R.T. and Boyd, R.N. Organic Chemistry. Allyn & Bacon Inc. Boston, 1974.
4. Windholz, M. et al., ed. The Merck Index. 10th ed. Merck & Co. Inc., Rahway, N.J., 1983.
5. Durrans, I.I. Solvents. Chapman Hall. London, 1971.
6. Drawford, D.L., R.O. Sinnhuber and H. Aft. "The effect of methylation upon the antioxidant and chelation capacity of quercetin and dihydroquercetin in lard substrate". J. of Food Sci. 26 (1961): pp. 139-145.
7. Gallo, D.P. "Methyl bromide, ethylene oxide, and ethylene formaldehyde: biological and toxicological problems and problems related to treatment of library materials". Nuovi Annali d'Igiene, F. Microbiologia 29(1) (1978): pp. 51-82.
8. Anon. "Ethylene oxide, ethylene chlorohydrin, and ethylene glycol. Proposed maximum residue limits and maximum levels of exposure". Dept. of Health & Welfare Food & Drug Admin. Docket No. 77N-0424. Federal Register Vol. 43, No. 122 (1978) Friday, June 23. pp. 27474-27482.
9. Anon. "OSHA Issues ethylene oxide standard". Art Hazards News 7(6) (1984): pp. 1-2.
10. Santarelli, R. "Procède pour la synthesis d'hydroxyethyl cellulose possédant une résistance améliorée à l'hydrolyse à catalyse enzymatique. Demande de brevet d'invention". No. 77-38429. Instit. Nat. de la Propriété Industrielle (2) (1979): pp. 412-570.
11. Sear, K.D., G.E. Ewing and G.R. Quimby. "Hydroxyalkylation strengthens high porosity pulps". Tappi. May 65(5) (1982): pp. 141-144.
12. Fraenkel-Conrat, H. The action of 1-2 epoxides on proteins. J. of Biol. Chem. 154 (1944): pp. 227-238.
13. Veis, A. "Intact collagen". In Chemistry of Collagen. Treatise on Collagen. Volume 1, edited by G.N. Ramachandran. Academic Press. London, N.Y., 1967.
14. Otterburn, M.S. "The chemistry and reactivity of silk". In Chemistry of Natural Protein Fibres. Edited by R.S. Asquith. Plenum Press, New York, 1977, pp. 53-80.
15. Watt, I.C. "The sorption behaviour of cystine-modified wool". Textile Research Journal, 33 (1963): pp. 631-638.
16. Bakerman, H., M. Romine, J.A. Schricker, S.M. Takahaski and O. Mickelsen. "Stability of certain B vitamins exposed to ethylene oxide in the presence of choline chloride". J. Agric. Food Chem. 4(11) (1956): pp. 956-959.

17. Windmueller, H.G., C.J. Ackerman, H. Bakerman and O. Michelsen. "Reaction of ethylene oxide with nicotinamide and nicotinic acid". J. of Biol. Chem. 234(4) (1959): pp. 889-894.
18. Windmueller, H.G., C.J. Ackerman and R.W. Engel. "Reaction of ethylene oxide with histidine, methionine and cystine". J. of Biol. Chem. 234(4) (1959): pp. 895-899.
19. Bares, M., M. Bleha, E. Votavova, J. Marek, E. Vachova and J. Zajic. "The reaction of fatty acids and their derivatives with ethylene oxide. V: A kinetic study of the second reaction stage of the reaction of stearic acid with ethylene oxide". Tenside Detergents 16(6) (1979): pp. 308-11.
20. Wesley, F., F.W. Rourke and O. Darbishire. "The formation of persistent toxic chlorohydrins in foodstuffs by fumigation with ethylene oxide and propylene oxide". J. of Food Sci. 30 (1965): pp. 1037-1042.
21. Gustafsson, K.H. "Residues of ethylene chlorohydrin in foodstuffs and in spices intended for industrial manufacture of foodstuffs". Vor Foda. 33(1) (1981): pp. 15-21.
22. Rajogopalan, S. and N.G.S. Gopal. "Ethylene chlorohydrin and ethylene glycol residues in ethylene oxide sterilized products". Indian of Pharmaceutical Sci. (May June, 1979): pp. 113-114.
23. Perkins, J.J. Principles and methods of sterilization in health sciences. 2nd ed. 5th printing. Charles C. Thomas Publ. #517, 1978.
24. O'Leary, R.K. The desorption kinetics of ethylene oxide from polyethylene, polypropylene and polybutylene. Ph.D. Thesis, Univ. of Texas, 1969.
25. Beard, H.C. and R.B. Dunmire. "Retention of ethylene oxide fumigant by shoes". Amer. Med. Assoc. Archives of Industrial Health 15 (1957): pp. 167-169.
26. Kowalik, R. "Some aspects of microbiology of paper and parchment". In Wolfenbutteler Forschungen Vol. I, Band I Jacobi Verlag. Kassel, Germany, pp. 61-90, 1977.
27. Vero, B.L., N. Marabelli and M.Z. Plossi. "Investigation of the disinfection by ethylene oxide of illuminated parchments". The International Council of Museums Committee for Conservation. 7th Triennial Meeting Zagreb. 78/1/10 (1978): pp. 1-18.
28. O'Leary, G. Isoelectric focussing, personal communications, 1986.
29. Loy, T.H. "Prehistoric blood residues: detection on tool surfaces and identification of species origin". Science 220 (June 17) (1983): pp. 1269-1271.
30. Belliveau, J., G. O'Leary, P. Cello, C. Vecoli, L. Black and E. Schaffer. "Development of an isoelectric focussing analysis to identify the type of animal tissue in cultural artifacts, specifically Aleutian gut garments". Process Report II. Dept. Chemistry, Bio. & Anthro. Providence College, Providence, R.I., 02918, 1982.
31. Righetti, P.G. and A.B. Bosisio. "Application of isoelectric focussing to the analysis of plant and food proteins". Electrophoresis 2 (1981): pp. 65-75.
32. Florian, M-L.E. "The freezing process-effects on insects and artifact materials". Leather Conservation Newsletter, 3(1) (1986): pp. 1-13 and 17.
33. Florian, M-L.E. "Biodeterioration of museum objects". Museum Round-up. Fall, 1978, pp. 35-43, or Dawson and Hind 9(43) (1978): pp. 35-43.
34. Kopperi, D.F. and C.C. Bard. "Freeze/thaw cycling of motion-picture films". SMPTE Journal, 94(8) (1985): pp. 826-827.
35. Walker, I.K. and F.H. Jackson. "Equilibrium vapor pressure of wool". New Zealand Journal of Science, 16 (1973): pp. 481-501.
36. Dehl, R.E. "Collagen: mobile water content on frozen fibers". Science, 170(3959) (1970): pp. 738-739.
37. Horne, R.A. Marine Chemistry. Wiley-Interscience. p. 364, 1969.
38. Cwilong, B.M. "Sublimation in a Wilson chamber". Royal Soc. of Lond. proceedings 190A (1947): pp. 137-143.
39. Thomson, G. "Relative humidity-variations with temperature in a case containing wood". Studies in Conservation 9 (1964): pp. 153-169.



40. Thomson, G. The Museum Environment. Buttersworth, 1978.
41. Lafontaine, R. Silica gel. C.C.I. Tech. Bull. No. 10, 1984.
42. Macleod, K.J. Relative humidity: Its importance and control in museums. C.C.I. Tech. Bull. No. 1, 1975.
43. Stamm, A.J. Passage of liquids, vapours and dissolved materials through softwoods. Technical Bulletin No. 929, U.S. Depart. of Agric., 1946.
44. Watt, I.C. and J.E. Algie. "Kinetic studies of the wool-water system. Part III: The mechanism of sorption of high water concentrations". Textile Research Journal, 31 (1961): pp. 793-799.
45. MacLaren, A.D. and J.W. Rowen. "Sorption of water vapor by protein polymers: A review". Journal of Polymer Science, 7(2/3) (1951): pp. 289-324.
46. Watt, I.C. "Kinetics of the wool-water system. Part II: The mechanisms of two-stage absorption". Textile Research Journal 30 (1960): pp. 644-651.
47. Kanagy, J.R. and J.M. Cassel. "Heats of wetting of modified collagen and other materials". American Leather Chemists Assoc., Journal, 52 (1957): pp. 248-259.
48. Carlene, P.W. "The moisture relations of textiles, a survey of the literature". Journal of the Society of Dyers and Colorists, 60 (1944): pp. 232-237.
49. D'Arcy, R.L. and I.A. Watt. "Water vapor sorption isotherms on macromolecular substrates". In Water Activity Influences on Food Quality, edited by L.B. Rockland and G.F. Stewart, 1981.
50. Hoadley, R.B. Understanding Wood. The Taunton Press, 1980.
51. Nyuksha, J.P. "Biological principles of bookkeeping conditions". Restaurator, 3 (1979): pp. 101-108.
52. Watt, I.C. "Water vapor sorption hysteresis in swelling substrates". In Physics of Materials, edited by D.W. Borland, L.M. Clarebrough & A.J.W. Moore. Commonwealth Ac. & Industrial Research Organization, Australia, 1979.
53. Watt, I.C. "Sorption of water vapor by keratin". J. Macromol. Sci. - Rev. Macromol. Chem. C, 18(2) (1980): pp. 169-245.
54. Sargent, C.M. "A brief history of materials in the Canadian Arctic" In Materials Engineering in the Arctic. American Society for Metals. Metals Park, Ohio, 1977.
55. Street, K.N. Fiber composite materials in an arctic environment. In Materials Engineering in the Arctic. American Society for Metals. Metals Park, Ohio, 1977.
56. Schirp, M. and H. Kubler. "Investigations on dimensional changes of small wood samples during cooling". Holz als Rohund Werkstoff 26 (9) (1968): pp. 335-341.
57. Kubler, H. "Shrinkage and swelling of wood by coldness". Holz als Rohund Werkstoff, 20 (9) (1962): pp. 364-368.
58. Sulzberger, P.H. "The effect of temperature on the strength of wood, plywood and glued joints". Aeronautical Research Consultative Committee, Dept. of Supply, Australia. Report ACA-46, 1953.
59. Comben, A.J. "The effect of low temperatures on the strength and elastic properties of timber". Instit. of Wood Science J., 13 (1964): pp. 44-55.
60. Beall, F.C. "Effect of temperature on the structural uses of wood and wood products". In Structural Use of Wood in Adverse Environments edited by R.W. Meyer and R.M. Kellogg, Soc. of Wood Sc. Tech., pp. 9-19, 1982.
61. Flanders, S.W. and W.N. Tobiasson. "Designing with wood for light weight air-transportable arctic shelter. How the materials were tested and chosen for design". In Structural Use of Wood in Adverse Environments, edited by R.W. Meyer and R.M. Kellogg, Soc. of Wood Sc. and Tech., pp. 385-397, 1982.
62. Taylor, M.A. Textile Properties. Forbes Publications, London, 1978.

63. Kreibich, U.T., F. Lohse and R. Schmid. "Polymers in low temperature technology". In Nonmetallic Materials and Composites at Low Temperatures. Edited by A.F. Clark and R.P. Reed, Plenum Press. pp. 1-33, 1979.
64. Hartwig, G. "Mechanical and electrical low temperature properties of high polymers". In Nonmetallic Materials and Composites at Low Temperatures. Edited by A.F. Clark and R.P. Reed, Plenum Press, pp. 33-50, 1978.
65. Sehgal, S.D. and R.A. Lindberg. Materials - Their Nature Properties and Fabrication. Kailash Publishers, 1973.



## SUMMARY

## TRADITIONAL TECHNIQUES FOR THE PRESERVATION OF CELLULOSIC ETHNOGRAPHIC MATERIALS

S.A.M. Monowar Jahan  
Keeper, Conservation Laboratory  
Bangladesh National Museum  
GPO Box 355 Dhaka Bangladesh

1. Introduction

In traditional society people are not aware of the preservation of artifacts and their households, however they generally employ some methods to ensure durability while objects are in the process of being constructed. The old techniques for seasoning wood or bamboo are still used in remote areas. Sap and the extracts of barks or fruits from different trees have long been in vogue as coating material in tropical countries of South-east Asia.

In the hilly region of the south eastern part of Bangladesh live the most colourful tribes, Chakmas, Tipras, Mags and Murangs. They collect wood, bamboo and cane from the green forest to make their households. Out of wood they construct houses, small boats and canoes and fashion grinding, husking and weaving equipment. From bamboo and cane they make baskets, mats and other big containers for storing cereals. Before making any objects out of wood and bamboo the tribal people usually immerse the wood and bamboo in water just after felling. Water submersion is not exactly a seasoning process, it protects wood logs and bamboo from insects and fungi. During water storage sugars, gums and tannins are partly leached out and as a result insect and fungi do not get sufficient food for their survival.

This process of seasoning or water storage helps to leach out soluble constituents and on subsequent drying the wood does not crack. The wood and bamboo is dried slowly under the shade of a tree or a thatched covering or by spreading straw, leaves, grass, rushes, etc. over them.

Gourd shells are widely used for making bowls, bottles, containers for salt, mugs, cups, spoons and musical instruments. Gourd is a kind of large fleshy fruit obtained from one of those plants that spread over the ground or climb by clinging to bushes, trees, etc. Its English name is Calabash gourd and botanical name *Lagenaria siceraria* (Molina) Standley. Locally it is called *Milok* or *Baaz*. Two types of gourd are used for making those items. The large gourds are edible. The other ones are the wild type, small in size and with a bitter taste. The smaller gourds are used for making small containers for water, and even small bottles about 5 cms in height can be made. For the construction of a special kind of wind musical instrument called *Khang* the rind of the small type of gourd and narrow bamboo pipes are used. This flute is a very popular musical instrument among the Murangs. In constructing stringed musical instruments gourd shells are common materials.

The main component of the gourd rind is cellulose. When the gourd is mature the shell becomes hard. For taking out the flesh portion from the hard shell cowdung and some salt are inserted into the flesh through a small slit. After three to four days salt and cowdung brought a chemical degradation in the flesh of the gourd by turning the whole flesh into curdy mass. Later this mass is drained out through the salt. Cowdung possesses bacteria which can digest cellulosic material secreting enzymes. Salt contains sodium ion which accelerates the degradation process. Most of the objects made out of gourd rind are from the wild type because it is bitter and less susceptible to insect attack.

Traditional tools for spinning yarn and weaving textiles are used by tribal women. Handloom textiles, carpets and blankets are outstanding for their design and weaving techniques. The roots or *Curcuma longa*, the leaves of *Indigofera tinctoria*, the sap of *Accacia catechouides*, the fruits of *Diospyros peregrina* and the bark of *Artocarpus heterophyllus* are used for dyeing textiles.

Fibrous bark from the tree known as *Sterculia villous* is used as ropes and string for constructing houses. The local name of the tree is *Udal*. This kind of bark is also commonly used for belts of baskets. A person can hang a basket on the back by fixing the belt upon the head during carrying.

A mixture of resin from plants, and wax from the hives of bees is a common ingredient for making adhesive. Wax from the hives of a kind of small fly is also found to be quite suitable for preparing adhesive. A mixture of resin and wax can be made by heating. After cooling, on exposure to air, it becomes hard and durable.

2. Treatment with extract from the fruit of *Diospyros peregrina*.

*Diospyros peregrina* is a medium tree with green leaves. Its English name is "wild mangosteen" and local name is *Gab*. Its bark is smooth and grey and its wood is grey with black spots. Flowering begins in April. The fruit is round with a diameter of about 4 to 5 cms. Generally it takes about one year to ripen the fruit. The unripe fruit gives a purple syrupy juice after



Khang. Musical instrument made out of gourd shell and bamboo.



Bark of *Sterculia villous* is used as a belt for baskets.





Diospyros peregrina (Gab).



Traditional husking equipment for beating Diospyros peregrina (L. name Gab).



Twii. A container for water made out of gourd shell.

beating or chopping.

The major component of the fruits are tannins, gummy substances and water. When the fruit ripens, tannins disappear. These tannins are a complex mixture of glycosides of various polyphenals and have strong reducing characteristics, as they reduce Fehling's Solution rapidly. It forms deep blue to black colour with ferric chloride and hence it indicates its pyrogallol nature. The tannins in the fruit are hydrolyzable and water soluble. Because of its antiseptic properties, the fruit is free from fungal and insect attack.

The period between December and January is the best time for the collection of the green fruits. After collection, the fruits are beaten with the traditional husking equipment and kept covered in an earthenware vat with a little water. After two or three days the purple coloured syrupy extract is used as a coating material for all household artifacts made of wood, bamboo, cane and gourd shells. It is applied to the surface of the object with a piece of cloth dipped in the extracted solution. Baskets and containers made of cane and bamboo are also treated with this extract. Husks of rice are mixed with the extract (as filler) so as to get a thick coating. It has very good indoor durability and consolidates the surface of wood and bamboo by penetration into the cells. After constructing a new boat or canoe, a coating of the extract is generally applied and cracks are also filled with the extract and with rice husks. On drying, evaporation of water and polymerization of the ingredients of the extract occur, giving a suitable coating. In the open air the coatings are degraded by the action of water. Household materials and other objects used in the open air are therefore coated periodically.

Yarns are soaked in the solution to make them stronger, and fishing nets are given successive soakings to protect the yarn from decay. Sometimes in order to dye the yarn dark black, iron beads are put into the solution which is heated for some time.

Tannins are abundant in other fruits and barks. The extracts from the barks of Diospyros peregrina and mahogani are also used as coating materials. The extracts are obtained by boiling the bark in hot water.

### 3. Washing of textiles with indigenous solution.

The ashes of bamboo shoots, banana plants, fruit shells of Bombax ceiba and other plants, fruits and leaves are used for cleaning textiles. The young yellowish green shoots form Bambusa tulda, a variety of bamboo, are cut into pieces and dried. After drying these are burnt. By dissolving the ashes in water, a solution of non-volatile inorganic constituents can be obtained. This solution contains soluble salts of sodium, potassium and other inorganic salts. It is filtered and the filtrate is used for cleaning textiles. The use of ash from bamboo shoots and banana plants is most common. The soapnut or the Sapindus trifoliatus is also used for cleaning textiles. After breaking, the fruits are kept immersed in water for thirty minutes. When lather is formed, the solution is used as a detergent.

### 4. Preventive Conservation.

Most of the cellulosic artifacts made by the tribal people are generally stored in the kitchen. In order to protect them from damp, baskets, Twii (a container for water made out of a gourd shell), musical instruments and other objects are hung from the roof so that they are held above the floor. When fire is kindled, the exposure of artifacts to the heat and smoke prevents the attack of micro organisms and insects. The products of wood combustion, (volatile organic and inorganic materials) are deposited on the surface of the stored objects forming a thin layer of brown patina. This patina is beautiful and harmless and serves as a protective coating.

A thin plaster of cowdung and mud is applied to the fence surrounding the house, and to bamboo containers and winnowing materials as a moisture retardant.

To prevent insect attack of textiles, the leaves of Melia azadirachta are kept in the folds of the textiles. Vernonina anthelmintica a kind of black seed is also spread through the textile container for protection against insects.

### 5. Conclusions

The object of this paper is to collect information regarding various traditional methods and techniques of preservation of artifacts. All the methods discussed above are very simple and old. This is a preliminary study; a complete study will give us a detailed picture of all the indigenous preservation methods applied to other types of materials. A scientific study of these preservation techniques may; show them to be suitable for application to artifacts.



## APPLICATION OF A NEW TYPE OF PYRETHROIDAL COMPOUND ON ETHNOGRAPHIC TEXTILES

T. Morita

National Museum of Ethnology, Expo-Park 10-1,  
Suita-Osaka 565 Japan

Y. Tujii

Nara Women's College, Kita-uoya Nishi Machi,  
Nara, 630 Japan

T. Matsunaga

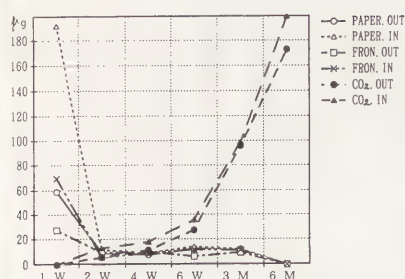
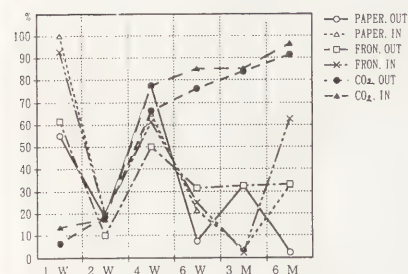
Central Laboratory of the Sumitomo Chemical Co.  
(Pesticides Dept.), 4-2, Takatsukasa-cho,  
Takarazuka, 665 JapanFigure 1. Quantities of Residual Chemicals ( $\mu\text{g}/\text{cm}^2$ )

Figure 2. Lethal Ratio of the Larvae (50 days old)

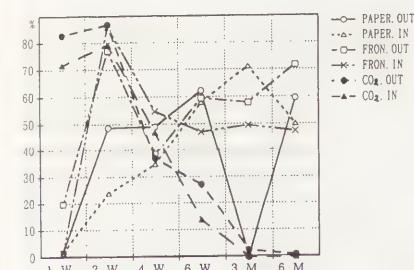


Figure 3. Damage Ratio by the Larvae

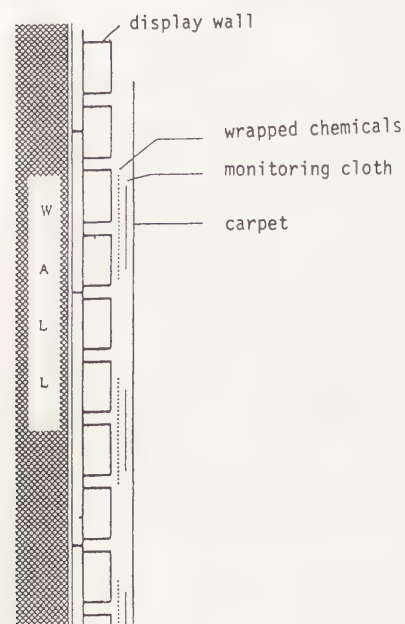


Figure 4. Position of chemicals and monitoring cloth on Carpet (section)

## 1. Introduction

Damage by moth-pests is a serious problem in ethnographic museums. In particular, larvae of *Linea Pellionella* (L) eat large quantities of dry animal hairs, including wool, fur and feathers. They prefer to eat less treated materials, that is less degreased or less industrially processed ones. When we put the larvae into a petri dish with two fragments of wool, one native and one industrially treated most of them gathered on the former.

Tujii has observed that a moth larva eats about 11.98 mg of wool in 50 days at 30°C and 55 + 15% RH. Few eat at below 10°C. Below the freezing point of water or under very dry conditions the pests find it difficult to move or live.

Some ethnic groups such as nomads of the dry Central Asian high lands or arctic hunters such as the Inuit have less need to consider special protection from pest attack because of the severe climate. However, a modern ethnographic museum with an air-conditioned climate and delicious foods is a paradise to the insect.

We have less fear of moth beetles because they require some weeks of very cold climate to hatch. Comfortable conditions to the moth are uncomfortable to the beetles.

We know the fumigation method utilizing methyl-bromide vapor is very effective, and our experiences show that even as a low concentration as 5 g/m<sup>3</sup> is sufficient to kill the *Tinea Pellionella*. But application of this toxic gas with high vapor pressure is only permissible within air tight areas such as fumigation chambers and not in open space such as exhibition halls. The fumigant is very strong but has no residual effect.

Many kinds of insecticides and insect repellents have been used such as camphor, para-dichlore-benzol (PDB), DDVP, etc. Toxicology of the effective DDVP is still unclear and discussions continue. Tujii revealed recently that PDB gas in low concentration does not act as a repellent but as an attractant to the moth-pest.

## 2. Used Chemical Compound

Chemical Name: d-Emperthrin or (RS) 1-Ethynyl-2-methyl-2-pentyl  
(1R)-cis, trans-chrysanthemate

Trade name : Vaporthrin

Manufacturer : Sumitomo Chemical Co. (5-15, Kitahama, Higashiku,  
Osaka, Japan)

An extract from the technical data supplied by the manufacturer is in the Appendix.

Three types of formulated chemicals were used for the test.

- 1) filter paper impregnated with the chemicals ( $5\text{g}/1500\text{ cm}^2$ )  
(sheet type)
- 2) 10 w% solution with Freon 11/12 (1:1) gas (spray type 1)
- 3) 10 w% solution with liquid carbon dioxide (spray type 2)

## 3. Experiment 1 - Enclosed spaces

The above three forms of the chemicals were applied to individual textile storage chests (each with a capacity of 2.06 m<sup>3</sup>) to determine the effect of the chemicals in an enclosed space.

## 1) Preparation

Three chests, each containing about ten articles of clothing, were used for the experiments. Clothes were hung in the usual way. For each chest, ten check points were selected as follows.

- 2 outside each of two items,
- 2 inside or in pockets of each of two items,
- 1 on the ceiling of the chest,
- 1 on the floor of the chest,

Six pieces of pure wool cloth (10 x 10 cm) were fixed on each check point. These were periodically analyzed to determine the level of residual chemicals.

To test the killing effect ten larvae of 50 days old *Tinea Pellionella*(L) on a piece of pure wool cloth were placed in a tee filter cage and were placed on each test point. One set of larvae was used as a control. The larvae were recovered seven days after the setting.

## 2) Dosage Method

5000 mg of the chemicals were applied to each chest and the doors carefully closed.

- Filter paper type: 2 pieces of the paper (15 x 50 cm each) were attached to the ceiling of a chest
- Spray types: quantities were determined from the spraying time, using the result of preliminary testing.

## 3) Recovery term of the test pieces

Recovery and analysis of the 6 test pieces were carried out after 2 hours, 2 weeks, 4 weeks, 6 weeks, 3 months, and 6 months after dosage. The insects were introduced 2 hours after the dosage and recovered 7 days after.

## 4) Quantitative analysis of the residual chemicals

Recovered cloth samples were washed in acetone to extract the chemicals and the solution analysed by gas chromatography (Shimadzu GC-7APE + ECD Detector).

## 5) Determination of killing or repellent effect

Three methods were used, the first to measure killing effect and the second and the third to find the repellent action.

- The number of dead larvae were counted.
- The total weight of living larvae in each cage was determined before and after the exposure.
- The weight of cloth in each cage was determined before and after the exposure.

It is understood that protection requires only an adequate repellent effect without necessarily having complete killing strength.

## 6) Results

Results of the tests are shown in Figure 1 (Quantities of residual chemicals), Figure 2 (Lethal ratio of the larvae), and Figure 3 (Damage ratio by the larvae).

Each value is an average of all the samples under similar conditions according to type and position of dosage.

Ratios were derived from the following equations:

$$DR = \left( \frac{\text{lost weight of the samples}}{\text{the initial weight of the samples}} \right) \times \left( \frac{\text{initial weight of the control}}{\text{lost weight of the control}} \right) \times 100$$

$$LR = \left( \frac{\text{numbers of dead larvae}}{\text{the initial numbers}} \right) \times 100$$

DR : Damaged Ratio

LR : Lethal Ratio

As shown in the Figures 1, 2, and 3, the results indicate that a residual chemical level of more than 25-30 mg/cm<sup>2</sup> gives a damaged ratio below 20 %, and a level of more than 100 mg/cm<sup>2</sup> gives a the lethal ratio over 80%. A residual level on the cloth of 25-150 mg/m<sup>2</sup> provided good protection from damage and a level of 150-200 mg/m<sup>2</sup> gave complete protection.

From the manufacturer's laboratory data complete lethal density occurs at more than 7 mg/cm<sup>2</sup> for the adult moth-pest, more than 25 mg/cm<sup>2</sup> for the newly hatched larvae and more than 250 mg/cm<sup>2</sup> for all larvae. More than 150 mg/cm<sup>2</sup> of residual chemicals on the cloth provides complete protection from moth damage. The outline of our results corresponds principally to the laboratory data.

Temporary rise in lethal ratio which appeared at the fourth week after spraying (both CO<sub>2</sub> and Freon) was probably caused by retranspiration of previously coagulated vapour. A similar effect was observed with the paper type at a later date, particularly at sites close to the pape.

Dosage by spraying is most effective within one week and effective two to four weeks after treatment, at normal room temperature.

The effectiveness of the impregnated paper begins from the fourth week and continues to the sixth month. Although no measurement were taken after this, the residual chemicals in the filter paper was only 0.006 - 0.0003% of the original which would have little effect.

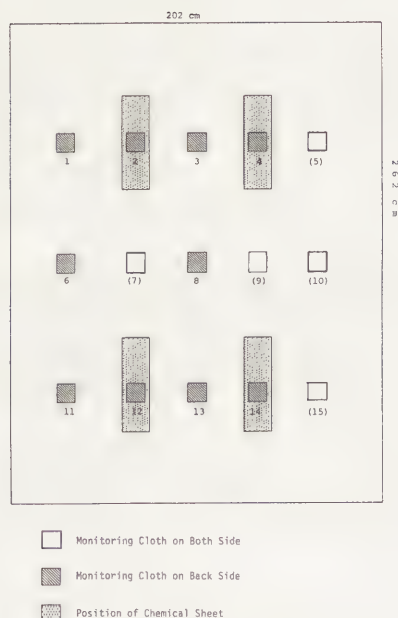


Figure 5. Position of Chemical Sheets and Monitoring Cloths

Pos. 1 (2)	DEPOSITS OF CHEMICALS (*)				Resid. wt. of Chest after 1W
	1 M	2 M	4 M	6 M	
1 surf	—	—	—	—	
2 surf	***	***	***	***	20.92 mg (*)
3 surf	—	—	—	—	
4 surf	***	***	***	***	124.59 mg (*)
5	—	—	—	—	
6 surf	—	—	—	—	
7	***	***	***	***	
8 surf	—	—	—	—	
9	***	***	***	***	
10	—	—	—	—	
11 surf	—	—	—	—	
12 surf	***	***	***	***	114.79 mg (*)
13	—	—	—	—	
14 surf	—	—	—	—	
15	—	—	—	—	425.24 mg (*)

\*) \*\*\*\*\* >200, \*\*\*\* 200-150, \*\*\* 150-25, \*\* 25-7, \* <7  
 \*) Initial weight of the chemicals in dosage paper : 2500mg  
 \*) Positions 2, 4, 12, and 14 are just on the chemical sheet

Figure 6(a). Quantities of the Residual Chemicals on a Carpet (semi closed space)



7) Observation of the effect of the spraying on insects

Within ten minutes of spraying all adult moths and newly hatched larvae were killed in situ. Some young larvae in contact with the concentrated gas were also killed in their case. Larvae in contact with dilute gas left their cases within 30 minutes and eventually died. In very dilute gas some strong larvae survived but remained inactive. The authors did not observe any effect on the egg.

8) Comments

- a. When the CO<sub>2</sub> spraying is used with a high RH and very low temperatures the gas forms a mist and will settle more quickly.
- b. Use of the CO<sub>2</sub> spray method may trigger a smoke detector.

4. Experiment 2 -- Semienclosed spaces

The application of the chemicals to a semienclosed or very narrow space, such as between a wall and a hung tapestry, was tested. The sheet type of the chemicals was used.

On a temporary display wall, set at a corner of a storage area, a piece of Persian carpet (about 200(w)cm x 260(h)cm) was placed. The microclimate of the storage was about 25°C and 58% RH with 25-30 cm/sec of air current. Four pieces of the chemical sheet (25 mg/15x50 cm) and 15 pieces of wool cloth (10x10 cm) were attached on the back, and 10 pieces on the surface of the carpet. The chemical sheet was wrapped with thin nonwoven cloth so that it did not directly touch the exhibited materials. Two kinds of wrap sheet, dark gray and white, were prepared for future use to match the hue and value of an exhibited object. The positions of chemicals and monitor cloths are shown in Figures 4 and 5. The test method is the same in principle as the experiment 1.

Measurements were made one, three and six months after the dosage.

Results of the experiments are shown in Figure 6. As the figure shows, the area of direct contact of the carpet with the paper is protected from the first month until the sixth month by full vapor of high density with sufficient killing effect, and the opposite surface has also a rather high density of vapor which gives adequate protection from insect damage. Both sides of the carpet at Position Numbers 1, 5, 6, 10, 11 and 15 were little influenced by the application --- the authors assume that the vapor may have leaked out into open space. Middle points in the vertical direction of the two dosage positions (7 and 9) also showed rather high density of the chemicals; however, those in horizontal positions 3 and 13) were covered with extremely diluted and almost ineffective vapor.

The cross point of Position Number 2, 4, 12 and 14 (that is No. 8) also shows a low density of residual gas. The phenomena may indicate that the main movement of the vapor does not go in the horizontal direction but only in the vertical direction. It diffuses slightly diagonally, but penetrates and passes through the normal thickness of a carpet.

Secondary evaporation or re-evaporation from the deposit of chemicals shows the same movement. Spaces with even a micro air current may allow a leakage of the vapor, so that inevitably low concentration occurs at the edges. However, perfect protection with concentrated gas is required especially at the center of the back side because the insects prefer darkness.

Our conclusions from this test are as follows;

- a) Direct contact between wrapped chemicals and the surface of wool cloth gives good protection from moth attack.
- b. Effects on areas not directly contacted by the chemicals vary depending on the position of the chemical sheets.
- c. Even a micro air current allows leakage of the vapor.
- d. The vapor moves mainly in the vertical direction and not horizontally.

If long strips of impregnated paper were placed horizontally on the backside less than 70-80 cm apart, better protection may be given to the whole.

5. Experiment 3 -- Semi-open spaces

Six months of field tests were done in the galleries of the National Museum of Ethnology, Osaka, using the same methods as outlined above. Micro climate condition of galleries is, in principle, almost the same as that of storage, but not as stable. Between 40 and 50 cm/sec. of air current is always detectable on the surface of exhibited objects. Samples of wool cloth were removed every two months after the dosage, and its effect was checked using insects at the fourth and sixth months. Results are shown in Figures 7 and 8.

At the end of the second month, there were distinct differences between the amounts of residual chemicals detectable in open spaces and in semi enclosed or semi-open spaces. After four months, effective residues were found only in a show case at areas of direct contact between the wool cloth and the chem-

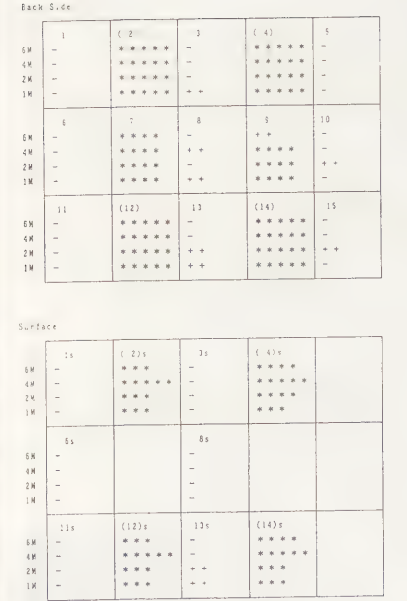


Figure 6(b). Topological display of the figure 6(a)

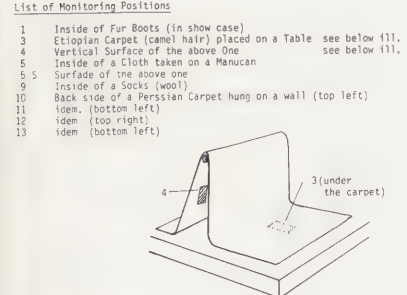
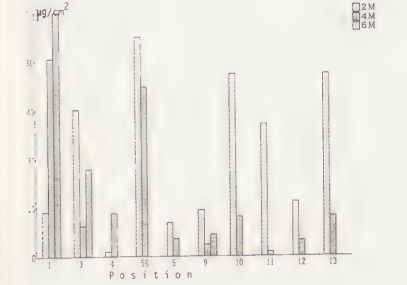


Figure 7. Quantities of the Residual Chemicals (semi open space)

icals. Except for a sample kept in a show case, one placed on the inside of a wool stocking, and one placed under a carpet on the floor, no residues were left at the end of the sixth months.

Damage Ratio (DR) by insects shows poor protection at the end of four months; however, we missed the DR data at the end of the second months. Considering the DR with residual quantities of the chemicals, 2-3 months of protection, in general, might be estimated under such conditions.

#### 6. Experiment 4 --- Open spaces

Vaporthrin diluted with Freon Gas was applied to a big tent of the Kazakh which is reconstructed in a hall of the National Museum of Ethnology. The climatic conditions were the same as in experiment 3. The dosage quantities were 3-4 g/m<sup>2</sup> and were measured in practice by jet time from a spray nozzle, after a calculation and results of pre-jet-test.

A check of the residual amount of the chemicals was made one hour, one week and two weeks after the application; however, no bio-test was done. Data from the one hour check revealed that the floor had a very high residual value probably because a large amount of mist descended and every surface had sufficient amounts to kill the larvae, except for the insides of folds or pleats.

One week after the dosage, however, the value became very low and was sufficient only to kill adult and newly hatched insects. After two weeks no protective effect was noticeable. (see Figure 9 and Table 1)

#### 7. Effects On Materials

Direct contact between the chemicals and copper (including copper alloys and compounds) may produce a chelete-like compound, the composition of which is still unclear. This forms a pale brownish and transparent layer on the surface of the metal.

In addition, when the concentrated vapor is enclosed in a narrow and cool space (such as between the hairs of fur or inside boots) the oversaturated dew may form a dark, sticky spot on the object. All of these by-products are easy to remove with diluted methanol. Other disadvantages have not yet been found.

#### 8. Conclusion

Vaporthrin is effective in protecting ethnographic objects from moth-pest attack under the following conditions:

1) In an air-tight space, such as in a closed chest or showcase, application of 5 g/m<sup>2</sup> of the chemicals is effective for about 6 months, at least as a repellent.

- The chemicals impregnated on filter paper have a reduced effect approximately 4 weeks after application.
- The chemicals diluted in Freon gas or in liquid carbon dioxide show very quick effects, which diminish continually 4-6 weeks after treatment.
- It is desirable to use the sheet type in combination with the aerosol. This is particularly important in opaque containers such as wood and metal which provide an ideal dark environment for the insect and which are not readily inspected from the outside.

2) Continuous effect depends on the air tightness of the space. In a semi-closed space, the sheet type will be effective as a repellent for about 3 months. The authors believe that an important condition is not so much the killing effect, but the repellent one.

3) In an open space, only quick killing or the "knock-down effect" can be expected from the 5 g/m<sup>2</sup> application of the aerosol. It may be possible to replace fumigation with the highly toxic methyl bromide or ethylene oxide with the use of the low toxic mist. If the Vaporthrin is applied twice during a 10 day period, it provides a comparable result.

4) The vapor moves in a vertical direction, therefore the sheet type should be placed in strips at regular intervals parallel to the horizontal.

5) Direct application of the chemicals to copper should be avoided because of the rise of dark staining. If this occurs the stain can be removed with dilute methanol. Overapplication in small enclosed spaces should be also be avoided.

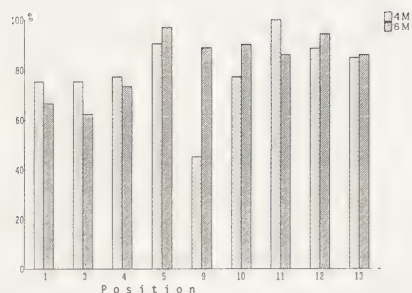


Figure 8. Damage Ratio of wool cloth (semi open space). Position numbers are the same as the Figure 7

Position	2 Hours	1 Week	2 WEEKS
1	112	72	< 7
2	301	15	9
3	646	18	16
4	162	77	50
5	2170	47	< 7
6	560	13	< 7

( mg/100cm<sup>2</sup> )

Table 1. Quantities of the Residual Chemicals on a Kazakh Tent (wool felt)

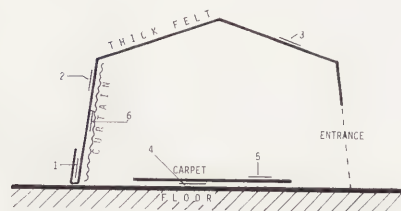


Figure 9. Position of Monitoring Cloth on a Kazakh Tent



## SUMMARY

The conservation of Japanese scroll-rolls has always been performed by Japanese conservators in accordance with their traditional methods.

Very few museums in Europe and U.S.A. have departments with Japanese specialists for the conservation of these objects. The National Museum of Denmark is not one of them.

The authors present here a case story on which the complete conservation (dismounting and remounting) of a Japanese "Kakemono" has been carried out, joining the traditional materials and techniques with a modern Western methodology: the use of the low-pressure apparatus.

N.B. The Japanese terminology has on purpose not been used in order to simplify the understanding of the text.

## THE CONSERVATION OF A JAPANESE "KAKEMONO" USING THE LOW-PRESSURE APPARATUS

Puccio Speroni and Karin Vestergaard  
Painting Conservation Department  
National Museum  
Bevaringssektion  
Brede, 2800 Lyngby  
DENMARK

Introduction

In the Western world, Japanese art, theater, music and visual art is generally considered as a matter of simple exotic curiosity. The art of hanging scrolls or "Kakemono" is not an exception to the rule. On the other hand, very little is known about how and why the scroll-rolls are built. This leads to the question on how a Japanese Kakemono can be conserved.

Very few museums in Europe and U.S.A. have conservation departments with specialists trained in Japan. The National Museum of Denmark is not one of those museums and when we accepted the task of conserving a Japanese Kakemono we agreed upon a compromise. We chose to use the traditional Japanese materials and techniques, but not the traditional methodology.

The National Museum of Denmark organized an exhibition in which a Japanese Kakemono was borrowed from the Östasiatisk Museet of Stockholm. This particular Kakemono dates from the 15th century and represents Prince Shotoku (575 - 622) who was the man that introduced Buddhism to Japan and translated many of its texts.

The Kakemono was in rather poor condition and, when the exhibition was over, we were asked to conserve it. This is its case story.

Structure Description

Prior to the conservation, the Kakemono measured 70X151cm of which the middle picture section itself measured 50X121cm. The picture area is painted on a very fine silk of a warm brown color. It is carried out in both watercolor and tempera techniques with vegetable glue as binding medium. The underlying paint layer is done in watercolors. On top of this, the details, such as the dresses, faces and lotus leaves, are painted in tempera. The picture is carried out in brown earth colors, green earth, lamp black, cinnabar and white. Additionally many details are painted with binder and gold powder as pigment.

This middle painted section is mounted in a silk brocade frame which consists of three parts:

- A) At the top and bottom of the painting are two strips of light brown silk with gold brocade, woven in with gilded paper.
- B) The first frame around the picture is a rose brocade decoration done in gray-yellow silk woven in with gilded paper.
- C) The second frame is a chrysanthemum brocade decoration done in indigo-blue silk woven in with gilded paper.

The middle picture and the two silk frames are mounted together on the reverse side by glued on strips of silk brocade. These strips have twofold purpose of connecting and underlining all the different parts of the Kakemono.

The Kakemono is laminated with two layers of Japanese paper glued together with wheat starch.

Previous Conservation

The Kakemono has undergone two previous conservations. The last took place in Sweden in 1930 by a Swedish bookbinder. Although the coat of paint and supporting foundation were most likely weak and decomposed then, the Swedish intervention did not result in any amelioration on this point. The bookbinder cut off some of the silk brocade frame in the upper and lower part of the Kakemono and glued a brown cartridge paper on its reverse side. While this lamination was still damp, the silk brocade edges were glued to a stretcher, putting an incredible amount of tension on the materials while drying. The resulting tautness harmed the picture.

The first conservation was performed in Japan by the Japanese in accordance with their country's traditional conservation principles. The Kakemono was completely dismounted during this restoration. The present silk brocade frames were undoubtedly mounted then as it was very normal for Japanese conservators to replace damaged fabric with new fabric.

The original layers of paper were totally removed from the reverse side of the painting. The large ruptures and holes in the painted silk present at that time were mended with pieces of silk. The silk patches were of almost the same quality and color as the original silk. Aside from the silk patches, the reverse side was supported with a first layer of gray paper. On this lamination, small



Figure 1 - The Kakemono prior to conservation. Raking light.

strips of white paper were applied in exactly those places where the original silk was torn, ruptured and weakened, and thereby the structure was reinforced at the same time. Finally, the entire Kakemono (the silk brocade frame and the picture area) was laminated with a second layer of white paper glued with wheat starch.

#### Description of the Present Condition

The silk support of the picture area was very decomposed. It was tender, brittle and broke at the least strain. It was frayed and full of cracks and ruptures. In some parts, as where the black color was used, the silk was completely decomposed and powdery which most probably was due to the large amount of binder needed for the lamp black pigment. Taking into account the entire picture surface, the silk was poorly bound to the underlying layers of paper. The consequence of prior conservations was large sections shifted in relation to one another resulting in crooked and displaced lines and surfaces. Likewise, these earlier conservations resulted in large portions of the silk, then loose patches, being incorrectly placed and this, of course, affected the picture motive. This was especially the case in the upper area of the painting where the incorrect placing was noticeably seen by the crooked overlappings in the original silk. Some of the patches, dating from the Japanese conservation, were totally loosened.

The paint layer was in many places still intact, but the colors, especially where the tempera technique was used, were very weak and lacked binder. Large portions of the picture area were peeling together with the underlying silk causing many holes with missed picture.

Having had a rather large portion of the silk brocade frame cut off in both the upper and lower sections as well as having been mounted on a wooden stretcher, the Kakemono had completely lost its most important characteristic, that of a hanging scroll-roll.

#### Low-Pressure Apparatus

As we have tried to describe, the Kakemono was in bad condition and in strong need of conservation. We did a lot of research on how scroll-rolls are constructed, the original materials used and how the Japanese conservators treated this kind of object. Although we have a large experience in conserving different types of ethnographical paintings, it is impossible for us to emulate the Japanese conservators. Nevertheless, we sought to replace the lack of dexterity by means of the low-pressure apparatus.

The low-pressure apparatus is a table connected to an aspirator (vacuum cleaner) and where the upper surface consists of a perforated aluminium plate. The air aspirated through the perforated sheet creates a suction. In this way, it is possible to avoid the risk of distortions while treating a wet painting and at the same time dry it with the utmost confidence.



Figure 2 - The reverse side of the Kakemono prior to the conservation.

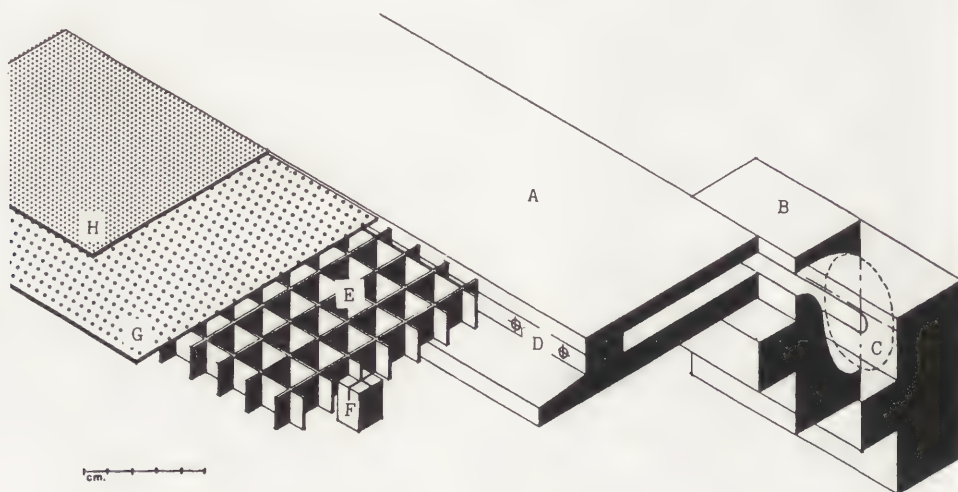


Figure 3 - Perspective section of the low-pressure apparatus:

- A) Hollow wooden frame. B) Connecting block. C) To the vacuum cleaner
- D) Air suction holes. E) Supporting aluminium grid. F) Spacer block.
- G-H) Perforated aluminium sheets.



### Treatment

The Kakemono was dismantled from the stretcher and the middle painting area carefully cut free from the silk frame. This was done as we intended to conserve the silk brocade frame separately instead of replacing it with new fabric. The picture area was placed on the low-pressure table with the front side up. The original silk fragments which were incorrectly placed were loosened by a very light dampening. Afterwards, they were placed in their correct positions which were determinable by the fractured surfaces, thread directions and color nuances. They were glued with wheat starch 1:2½ in water. Crooked and overlapping parts of the picture were likewise loosened, set in place and glued similarly.

The painted surface was then protected with a layer of very thin Japanese paper glued on with wheat starch 1:3 in water.

The picture was then turned around with the front side down on the low-pressure table. The brown cartridge paper from the Swedish restoration, as well as the white paper from the Japanese intervention, were manually removed dry. The gray Japanese paper with the white paper strips still remained on the Kakemono's reverse side. The strips were removed by dampening on the low-pressure table. The gray paper was likewise removed in the same way. The original reverse side of the silk was now exposed and the silk patches from the Japanese conservation removed.

In some areas, behind the black color, the silk was extremely weak and fragile, and quite a lot of fragments from the original silk were missing in the upper area. Furthermore, the entire silk support was rather transparent. In order to avoid laminating the painting with colored paper and replacing patches, we decided to reinforce the old silk support with a new layer of silk.

For this lamination we chose a slightly thinner silk than the original one. A color, one shade lighter than the original brown, was dyed. This color made both a good background for the thin, transparent original silk, as well as a good neutral color for the missing areas in the painting.

The newly dyed silk was stretched on a wooden frame and applied wheat starch 1:2 in water. It was then transferred to the picture's reverse side on the low-pressure table. With the help of aspiration and using a large tightly-haired brush, the silk was "dabbed" very close to the original support. After drying on the low-pressure apparatus, the painting, now laminated, was turned front side up and the previous paper protection removed. The extra edges of the new silk lamination were used to restretch the painting on a frame. Thus set up, the picture was allowed to rest and dry in tension for two weeks.

During this time we proceeded with conserving the silk brocade frame. The frame was placed reverse side up on the low-pressure table. The cartridge paper as well as the white Japanese paper were removed dry. Afterwards the silk strips which joined the frames together were removed by a slight dampening. In theory the frame's sections were now separated, but still locked in their position by the low-pressure aspiration force. The frames consisted of 46 pieces joined by small strips of Japanese paper or, in some place, by a thin overlapping. Before dismantling them piece by piece, a precise reconstruction on a scale of 1:1 was drawn. All the silk pieces were numbered in accordance with the numbering on the reconstructed drawing. After removing the final paper layer on the low-pressure table by means of dampening, each individual piece of silk brocade was laminated again with a new layer of Japanese paper and wheat starch 1:2½ in water. The Japanese paper was of the same qual-



Figure 4 - Detail prior to treatment. The misplacement of a fragment of the original silk support is clearly noticeable.



Figure 5 - The same detail after conservation.

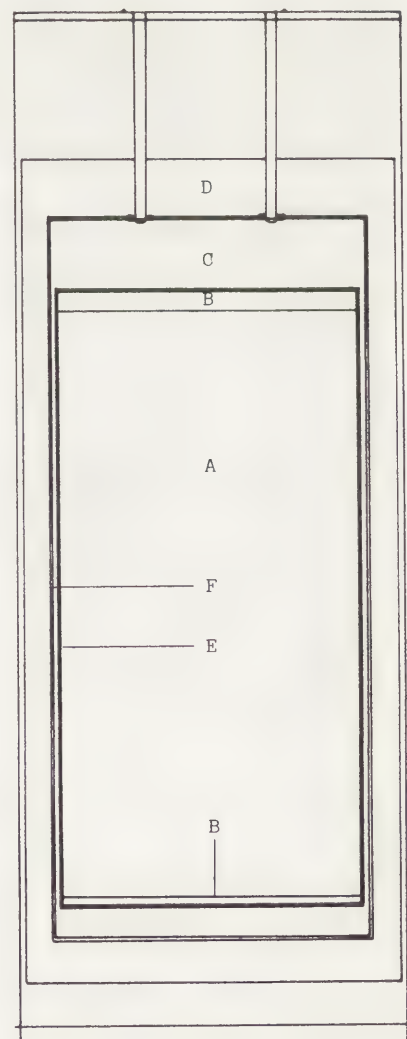


Figure 6 - Schematic drawing showing the dimensions of the Kakemono after conservation. The letters indicate the different parts of the scroll which are mentioned in the text.

ity and thickness as that which was used with the Japanese conservation. The edges on each piece were cut clean of any remaining paper and were now ready for remounting.

After two weeks of drying in tension, the picture section, while still setup on its stretcher, was laid down reverse side up on the low-pressure apparatus and laminated. "Kinugawa" paper and wheat starch 1:2 in water was used for this first lamination. While still damp, the paper lamination was dabbed with a brush and then allowed to slowly dry out on the low-pressure table. When dried, the picture was placed on an illuminator. By transillumination it was possible to discern where the original silk was torn or ruptured. Paper strips with wheat starch were applied to these weakened areas in accordance with Japanese tradition.

Based on the 1:1 chart of the framing construction done prior to the conservation, the silk framework was now reassembled. The vertical and horizontal frame parts were mounted individually. Each silk piece was joined together with paper strips on the low-pressure table. Joining of the frame parts to the picture area was begun from within. First part A to B, C and D. The frame parts were joined to one another and to the painting area on the low-pressure table by using previously dyed silk strips laminated with paper (E and F) and wheat starch 1:2 in water. This was precisely as it had been prior to our conservation.

As mentioned, the silk brocade frame was reduced, cutting off sections in both the upper and lower parts of the scroll-roll. We also had to cut off about 2cm from the sides because they were very damaged by the strong glue used when the Kakemono was stretched on the frame. To render the scroll to its original state and dimension, the indigo-blue prime color of the original outer frame was dyed onto a silk of the corresponding thickness. This silk was laminated with Japanese paper and wheat starch. This newly dyed frame part, recreating the Kakemono's original format, was added to the old frame's upper, lower and sides parts by means of small overlappings.

Finally, the entire scroll (picture area and framework) was laminated with a layer of "Kinugawa" paper with wheat starch 1:2 in water on the low-pressure apparatus.

The edges were trimmed so that the Kakemono had its original dimensions. By following Japanese instructions, it could be calculated what the original format must have been based on the innermost frame part B's measurements. A round pole was mounted to the lower edge while a semicircular pole was mounted to the top edge. Their diameter and length were also in accordance with the Japanese instructions.

It has been two years since the Kakemono of Prince Shotuko was returned to the Östasiatisk Museet in Stockholm. As far as we know, until now no alterations on the painting surface, or structure distortions or tears have been observed.

#### Bibliography

- Okudaira H., Emaki: Japanese Picture Scrolls.  
Tokio, Charles E. Tuttle, 1962.
- Van Gulik R.H., Chinese Pictorial Art as viewed by the Connoisseur.  
Istituto Italiano per il Medio e Estremo Oriente, Rome 1958.
- Toishi K., The Scroll Painting.  
In: Ars Orientalis, Vol. II, 1979.
- Hughes S., Washi: The World of Japanese Paper.  
Kodansha International Limited, Tokio 1978.
- Joyona M., Japanese Scroll Paintings: A Handbook of Mounting Techniques.  
Foundation of the American Institute for Conservation of Historic and Artistic Works, Washington, D.C. 1979.
- Hacke B., A Low-Pressure Apparatus for Treatment of Paintings.  
In Preprints, ICOM Committee for Conservation, 5th Triennial Meeting Vol. I, nr. 78/2/12. Zagreb 1978.
- Hacke B., Low-Pressure, Heat Moisture, Stretcher. Notes on Further Developments.  
In Preprints, ICOM Committee for Conservation, 6th Triennial Meeting Vol. I, nr. 81/2/8, Ottawa 1981.



Figure 7 - The Kakemono of Prince Shotuko after conservation.



## SUMMARY

## USE AND CONSERVATION OF A PABUJI PAR

This paper is one chapter of a large interdisciplinary study on the various aspects of the cult of Pabuji - a local deity worshipped in Rajasthan (N. W. India). The fact that it is part of a much greater project explains why names and other details are referred to with only little explanation. The main point here is the confrontation of Western approaches in conservation and restoration with the ways the object is approached, handled and treated in the context of the culture from which it originates. Dealing with conservation problems concerning non-Western objects provides a mirror that clearly reveals the preconceptions from which the Western and westernized conservation world tends to act.

Ernst van de Wetering  
Art Historian  
Central Research Laboratory for Objects of Art and Science  
Gabriël Metsustraat 8  
1071 EA Amsterdam, The Netherlands.

The juxtaposition of our twentieth-century Western approach towards cultural heritage with the attitudes of the past or of other cultures, is one which certainly offers an illuminating outlook on our behaviour in the museum-world. First of all it makes us aware of our most literal conservatism; our urge to stop Time from changing anything of the object in question. This urge is in - one could say - tragic contrast to the way in which objects, buildings etc. were in their original context, adapted to changing taste or function, or simply "used up".

This conservatism of ours, partly inspired as it is by an intense nostalgia, is also dictated by one of the fundamental ethical laws of Western science - the obligation to keep the sources of our knowledge as far as possible available for reconsideration of the facts. Seen from this angle our museums are storerooms for source-materials - a designation which seems all the more appropriate when one has been behind the scenes at, for instance, an ethnographical museum.

The permanent availability of the collected objects necessary to accommodate the ever-changing outlook of science and scholarship has its consequences for the approach adopted in the fields of conservation and restoration; that is obligatory documentation of each treatment; if at all possible reversibility of the measures taken; doing the minimum, but making the object at least intelligible and presentable if it has been distorted by accidents, by later interventions or by the slowly-gnawing teeth of Time.

In the following pages I shall juxtapose the way in which the Rajasthani Pabuji-singers (bhops) treat the cloth-paintings (pars) in front of which they perform, with the way in which one such par was treated in the Amsterdam conservation institute, where I work as an art-historian with a special interest in theoretical aspects of conservation and restoration.

The bhopo Parbu of Marwar Junction was asked: "When your par is no longer usable, what do you do with it?" Parbu answered, "It must be 'cooled' (thandi karno) by sinking it in Pushkar lake (a sacred lake in Rajasthan) or in Gujavo well (Pabuji's well in his village Kolu). This is what should be done - but in practice it may not be possible, and any good lake will do."

Here is one of the strange dilemmas in ethnography: whether one should be glad, or not, that a number of Western and Indian museums have been able to collect pars which, being no longer usable, should actually have been disposed of in a ritual way ('cooled'), instead of surviving in a museum. Parbu's comment on the purchasing of used pars does not put the blame on unethical collectors: "It is the bhopo's duty to 'cool' his par, but it is true that some bhops have become infected by greed and sell." One of these old, worn-out pars came into the collection of the Tropenmuseum of Amsterdam.

The par was indeed in a terrible state, in such a terrible state that, ignorant in the field of Indian art as I was when we received it for treatment at the Central Research Laboratory for Objects of Art and Science, I could at first easily believe that its antiquity was of the order of five hundred years, proposed on the basis of the (incorrect) initial reading of the inscription next to the main figure. One can imagine what a hilarious surprise it was when later, after chemical analyses of the (synthetic) red dye-stuff of an original part of the red band along the upper edge and repeated efforts to decypher the inscription, the par turned out to have been painted in the twentieth century, in 1907. But actually that should not have been a surprise as we knew by then how intensively a par is used.

This is what we found at our first confrontation with the object; an enormous, fragile rag painted with numerous figures, which was frayed and mutilated along the lower edge; torn at many places (mainly in a vertical direction); and at one place there was a big hole covered by a clumsily-applied rectangular piece of cloth, showing traces of a design that did not correspond with the design



Detail of Pabuji par



of the par itself at that point. Worst of all was the fact that, since the figures were incomplete on the right-hand side, a piece must be missing on that side which, as we later deduced from other pars, measured some five feet. Along the upper edge a red folded band was roughly attached, the band itself being mended and partly replaced at several points with pieces of more or less discoloured red cloth. When this red band was removed, it showed that most of the upper edge of the par was also missing, while the area that was covered by the band was severely mutilated. The whole thing was very dirty especially in the lower area, to such a degree that the representations of figures, animals, plants and buildings were difficult to make out; in the same area the painted surface was also partly abraded.



Detail of Pabuji par

All these symptoms of serious decay could later be understood as traces of intensive use when once we knew how this object had originally functioned. It is, however, not at all exceptional for a museum to offer an object for treatment without providing the results of any previous research on the function and material history of that object. This frequent omission is explained by the general misconception that the work of the conservator or restorer (as long as one does not have to reconstruct missing parts) is exclusively of a technical nature. In reality each decision concerning a treatment has factors of an interpretative nature. Very often preconceptions, conscious or unconscious, at various levels of interpretation - scientific, aesthetic, ethical, museological, psychological - influence decisions. In our case the omission to provide basic information at the very start of the project was understandable, as the painting had been bought from a dealer instead of being collected in "the field" after study of its function and use. (As later turned out, it was a very lucky purchase, the par being one of the best and earliest dated works of one of the finest Josi painters known to us: the legendary Jarav, who died in 1951, eighty years old.)

At first we did not even know that the painting had been used by an itinerant bard, we first supposed it to be a wall-hanging. This made us misunderstand the causes of deterioration which we thought to be the results of random accidents, and also made us misinterpret the repairs, which we considered to have been made by random tinkers. The revaluation of these symptoms of decay, and of the repairs and additions we found, will be the actual theme of this essay. First, however, I shall describe the project in general and indicate some of the dilemmas we faced; it will then be possible to evaluate the chosen solutions in contrast with the way the bhopos themselves treat their pars.

Little by little we learned to understand the par as a unity, a product of one craft, an essential attribute of another. It had been painted by a member of a sub-caste of painters, the Josis, who over generations have produced these paintings in a rigid tradition, following a now lost prototype, depicting scenes from the story of Pabuji, a local bhopo, who set the painting up wherever he sang and recited the epic at nightly performances. These traditions of painting and performing the epic of Pabuji are still alive.

This information we found in the documentary files of the Tropenmuseum and the Ethnomusicological Institute of the University of Amsterdam and was expanded with the help of my colleague Dr. Hartkamp-Jonxis. Many aspects of the object we had to treat we became only slowly aware of, mainly after having met two scholars who were in the course of doing field-research on Pabuji, the Indologist Dr. John D. Smith of Cambridge and the folklorist Joseph C. Miller Jr. of Philadelphia. But these meetings took place after the par had already been treated. Through the contributions of Joseph Miller our estimation of the importance of the par changed, as he knew the genealogy of the Josi painters and the place of the painter of our par, Jarav, in the tradition. Little by little, a rather long catalogue of pars painted over a period of nearly a hundred years was assembled, among which were some six painted over a period of 30 years by the painter of our par.

It was also only after the par had been treated that we finally came to understand the principles of its visual organisation which was determined not by the chronology of the epic but by the placing of the courts and villages in and between which the action took place. The interviews conducted by John Smith with the bhopo Parbu and the painter Srilal on my questions about the maintenance, repair, disposal etc. of the par took place five whole years after the actual treatment in the Central Laboratory.



It is worthwhile to reconsider the way we treated the par, and to see if and how the increase of our knowledge might have influenced our present judgment of the decisions taken in the conservation project. This evaluation is not inspired by any masochistic self-criticism, but rather helps to demonstrate the relativity of many of the seemingly objective considerations which guide the decisions taken in the field of conservation.

After the removal of later additions to the cloth, intensive experiments were undertaken to find out whether or not it could be cleaned by washing. It would have been interesting to know at that time that one of the constant worries of a bhopo is to keep his par away from moisture, and to have heard the bhopo Parbu's rather startling accolade of praise for the painter Jarav himself: "He was a truly great painter - you could hold his pars out in the rain and they wouldn't spoil." Anyway, with a slight sensation of risk the par was finally cleaned in a bath of demineralised water and weak soap.



Detail of Pabuji par

To follow the visible indications of how the bhopos who once used this par had tried to clean it was out of the question. They had, at some particularly dirty points, cleaned only the areas round the figures, thus strengthening considerably the silhouette effect of the still dirty figures against the now relatively lighter background. Partial cleaning with the result of changing the relative contrast of tonal values is however one of the taboos in western restoration. The whole object should either be cleaned evenly to a certain degree or be left as it is. So partial cleaning of the background was out of the question. Once we knew that the performances take place at night with the illuminating of a small open oil-lamp, we could well understand why it was undertaken by the bhopo. The silhouetting of the figures against a light background is, under such conditions, essential to distinguish them at all.

After this washing the visibility of the painting had increased a good deal. It was then attached to a textile support of about the same tone as the aged cotton on which the painting was done. The support was made to the size that the par must originally have been. The result was that great parts of the whole surface were now blank - the right-hand side, the hole, and long, irregular areas along top and bottom. Among our reasons for backing it in this way were that we wanted the par to be fit for exhibition in its original hanging position, and that it could be rolled and unrolled for storage and transport without risk. Making the support the original size of the par would, we thought, provide a better understanding of the object in its original shape without having to reconstruct it. I later felt this solution to be strongly influenced by similar, rather fashionable practices in Italian fresco restoration, and came to feel almost embarrassed. The introduction of these "neutral" irregular shapes introduces as many strange elements as a tentative reconstruction, if not more, and it forces one to remove the natural traces of decay that reconcile one to the inevitability of the tooth of Time. In an interview with the Josi painter Srilal, John Smith confronted him with photographs of the Tropenmuseum par after it had been treated in this way, and his response gave me some relief from my embarrassment. He said first that, if he had had the task of restoration, he would have put clean cloth over the bad parts and repainted them; but then he explained to his interviewer why we in the Central Laboratory had added the long cloth with its blank sections: "It's a good idea, for it shows how much is missing and fixes your centre of attention in the right place." That was exactly why we had done it.

But Srilal's approach, just like our own, is in the first place dictated by artistic considerations, and by the wish to give information about the original size and the original central position of the main Pabuji-figure. In fact, our blank additions and removal of the repairs (leaving the earlier damage clearly visible, and only safeguarding against future deterioration) had given the par an appearance which it had never actually had before. This way of preserving it came to seem almost like a kind of stylisation. The par had become a mummified ruin, the museological image of an actual object.

This feeling took hold of me when, during an exhibition, it became possible to confront our treated par with the 1898 par of the Victoria and Albert Museum. The appearance of the latter was similar to that shown by our Tropenmuseum par before treatment. By comparison, ours looked alienated. An important reason for this was that we had already removed the many traces of earlier repair



by the bhopos who had used the par. These repairs had been so disturbingly clumsy in our eyes, and to our feeling so alien to the object, that we did not hesitate long before removing them, as they obscured much of the aesthetic quality of the painting. There were also technical reasons to get them out of the way; since we planned to clean the par and back it with a supporting fabric they would be a hindrance. We first removed a multitude of crude stitchings which had been applied in order to close up tears in the cloth. We observed that the added rectangular piece of cloth considerably overlapped the edges of the hole which it was intended to cover, and we therefore took it off. (It turned out to be, in all probability, a fragment from the missing right-hand part of the par.) Next we removed the messy red band attached to the upper edge, chiefly because we feared that its colour would run when we came to wash the painting. At that time we also considered it to be another repair, a particularly disturbing one since it covered a long strip of the painting and because of the very intense red colour of its newer parts, which seemed to be in striking disharmony with the colours and the "patina" of the painting itself. We then removed the 15-inch-wide strip of cotton fabric that was attached for reasons which we did not at first understand along the right, mutilated side of the object.



Detail of Pabuji par

Apart from these repairs and additions to the textile, traces of previous restoration could also be found in the painting itself. The outlines of the two-and-a-half remaining companions to the right of the main figure were newly painted. The face of this main figure, its hand and some other details showed a brown discolouration obviously caused by overpainting with a substance which had proved to be corrosive. As mentioned above some small areas of the background which originally consisted of the white starched cotton fabric itself, now dark with dirt, had been cleaned.

The decision to remove some of the repairs and additions - the stitchings, the patch, the red band, the strip of white cotton - was basically guided by a typical Western outlook on works of art. Namely that the creator is far more important than the "consumer", so that the traces which the latter leaves on an object are fundamentally alien to that object. This outlook changed gradually as we acquired detailed information about the function of a Pabuji par. All the cases of damage could now be understood. They were no random accidents but rather the results of daily handling by the bhopo: - the rolling and unrolling; the right-hand side always being on the outside of the roll as it is carried about and so being exposed to serious wear; the tendency of the starched fabric - especially towards the outside of the roll - to crack "vertically" along the folds formed as the roll is flattened against the shoulder; the stretching with poles and ropes before the performance starts, with the aim of keeping the painting taut; the upper edge exposed to strong forces as a rope is pulled through the folded red band, which thus carries the weight of the entire painting and consequently needs frequent repair; the upper edge of the painting being perforated and so exposed to the risk of increasing mutilation; the touching and wiping of the long cloth over the ground during hanging and performance, resulting in dirtying, abrading and finally fraying of the lower area; the carrying around of the rolled painting from one performance to another, accumulating on the way dust from the Rajasthani desert; and the soot and smoke from the open oil-lamp used by the bhopo's clumsily-applied paint on face and hand of the main figure in the Tropenmuseum par might very well be an indication that this was such a bhopo retouching. We have since found such retouching, more or less competent, on many pars.

One can draw some conclusions from the way the bhopo restores his par with respect to the way he "sees" it. Although Parbu stated that an incomplete par cannot be used, it is obvious that pars have been used intensively and long after they had ceased to be complete. Possibly these were pars given to poor bhopos who needed one as seems to have been a habit, the point is that they were used. There is an agreement, doubtless accidental, between the fact that in an actual performance the last part of the story is often not sung and the fact that the right-hand part of the par can evidently be so easily dispensed with if it is missing. Though the story is not depicted in a chronological order "from left to right", it happens to be the case that the last section of the story "takes place" in the right-hand area of the par. So, just as there is an obvious indifference on the part of the bhopo and his audience with regard to narrative completeness of the oral epic, there is a similar indifference toward the iconographic completeness of the painted epic, the par.



Two cases in which we know that holes in pars have been patched over with pieces of pars support this last statement. What results is pictorial overcompleteness or confusion of the iconography. In both cases, pieces of a par - either the same or a different one - were taken whilst bearing discernible traces of the painted image, and attached as patches at positions away from their original context. In the case of a par ascribed to Kalyanmal in the Basel Museum für Volkerkunde this led to the duplication of a scene: Rupnath enters Jidrav Khici's bedroom to murder him ... twice. In the par we treated for the Tropenmuseum the patch was sewn over a hole in one of the companion-figures. The patch itself depicted a part of the pyre on which the widows of the deceased warriors commit ritual suicide (become sati). Pabuji's bride Phulmati can be seen immolating herself, yet as a patch, the fragment had been turned through 90 degrees and was vertical not horizontal. Considering the impossible case of a fainting Mary under the Cross being used to patch up a hole in a picture of the Last Supper emphasizes the peculiarity of such a bhopo repair in Western eyes.



Detail of Pabuji par

This observation about the bhopo's lack of concern for pictorial completeness or iconographic correctness - which I have tried to demonstrate here on the basis of the bhopo's approach to decay and repair of the par - seems at first not to be confirmed when we consider the fact that bhopos, sometimes being present when a new par is painted for them, may show through their request for the incorporation of certain scenes, a marked interest in the iconography. On the other hand the pars that some bhopos paint themselves differ astonishingly from the Josi pars which they try to imitate. They differ so widely among themselves that one is tempted to judge them as incredibly sloppy imitations in every respect, including iconography. Many scenes are either left out, reversed, or even put in the wrong place. But the central court is always present and so to speak correct; indeed it is the most commonly-retouched part of the par. The most striking demonstration of the unimportance of iconographic correctness is a known case where a bhopo recited the epic of Devnarayan in front of a Pabuji par. Again it is the central court which is important here, it is so similar in the two cases as to "make little difference".

All this adds weight to the conviction that a par is primarily a portable temple, whose mere presence (in whatever condition) is more important than pictorial completeness or iconographic correctness. The symptoms of decay and of consequent repair by the singers not only help to corroborate this conclusion, seen from this point of view they can now be understood as significant elements of the used par.

Another type of repair which we first tended to misinterpret, and now start to understand as a significant element of the par, is the very common replacement of parts of the red band along the upper side. This is usually stitched to the par by the bhopo himself, in order to hold the rope for the hanging and stretching of the par. It does not belong to the object when the painter hands it over to the bhopo. Dr. Smith asked the painter Srilal and the bhopo Parbu why the top band is always red. Srilal answered that this was because red is beautiful, whilst Parbu said, "Because red is the chief colour of the par. Another colour would not look good." The choice of red and especially this red, a very strong lake colour which does not in fact occur on the par, might however also have another explanation. It is used on every par we have encountered and must be of more significance than the mere choice of a personal taste generally shared by Josi painters and Pabuji bhopos. The same colour can be found round the borders of many Rajasthani miniatures - as long as these borders have not been matted away by Western framers of "good" taste who strive to increase illusionism with their bevelled "window" mats round the actual picture part of the miniature. This red seems to be the traditional framing colour, the choice of which must have more meaning than mere prettiness; Srilal called it an auspicious colour. The frequently-observed repeated repairs of the red band with the same colour indicate that this tradition is very strong.

We had at an early stage of the project found out what the function of the red band was, so it was replaced after the par had been backed. But it was not put back where we had initially found it, over the mutilated, incomplete upper edge but instead on its "original" location along the upper edge of the blank textile support which indicated the "original" upper edge. The many stitches that had been removed were not replaced, as the supporting fabric had taken over their function. The patch likewise was not put back over its hole. If we had been as "logical" with it as with the remounting of the red band we might

have returned it to its "original" place, where the widows' pyre is usually depicted, the patch thus becoming an absurd little rectangular island in the blank area at the right-hand side. As for the white cotton fabric which had been attached along the right-hand edge, it was not replaced since the five blank feet of the supporting fabric had replaced it. Sewing it to the end of that supporting fabric would have been meaningless.

It is clear that this treatment has seriously upset an organically-developed situation. In particular, it has disturbed the traces of use by the bhopo, and his measures to prevent the decay of his portable temple. It has removed a part of the indications of how he himself experienced this object. One could thus say that there had been a loss of material for ethnographic research, were it not that these indications were carefully documented. The gain from this treatment is that the par as a fragile object was protected much better for the future. As a painting it can now be enjoyed and studied much more satisfactorily. As a matter of fact this has proved a useful contribution to the art historical research to which it has already been subjected.

The undertone of self-criticism in this essay vis-a-vis the conservation project described, indicates that I am not as happy now as previously with the decisions that guided actual execution of this project. My reservations might be understood as resulting from a rather romantic approach towards one strange object that happens to have survived and found its way to Amsterdam. Such an approach could be held to account for the feeling of loss of a certain aura, the loss of any of the "radiation of authenticity" which one experiences, or seeks to experience, in confrontation with such an object. There is also what I consider to be a very concrete argument against the treatment we employed, which is that this object like many other objects of cultural value, has now been transformed from a venerable ruin in its own right, into a shape it never had before. It was adapted to our scientific and museological needs - and that is turning things upside-down.

In addition, it is important to realise that such treatment is also unquestionably partly inspired by an urge for tidiness and "quality", virtues which have a place in the kitchen but which should be suppressed in our dealing with objects in a museum. As Björn Hallström expressed it:

"Rising living standards are apt to induce us to exaggerate our requirements of material quality, so that we become hysterical when confronted with what we regard as defects but which, in fact, are no more than a natural symptom of age. Left to themselves, the processes of ageing at work in an old painting are often exceedingly slow ... Conservation may equally well trigger new processes of decomposition - with unexpected consequences." (F. Makes and B. Hallström, Remarks on Relining, Stockholm 1972, p. 43.)

It is not merely that one would rather do, optically, the minimum to an aged and weakened object. Any radical treatment will rob it of one of its most essential aspects - its authenticity as a remnant, a "messenger" from the past.



## SUMMARY

This project describes the freeze-drying of recently-collected Eskimo artefacts made of skin and fur, some of which were damp on arrival at the British Museum. An assessment of the success in retaining shape and flexibility was made by comparing them with similar articles which had been allowed to air-dry.

In a series of complementary experiments, a number of samples of skin and gut were also freeze-dried after pre-treatment by humidification, and in a variety of commonly-used humectants. Changes in appearance, dimension, weight and flexibility were noted after freeze-drying and compared with air-dried samples and with the controls. Results of the tests are recorded and discussed and proposals made for further research.

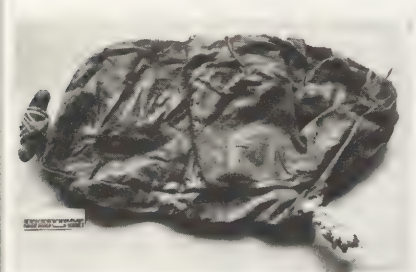


Figure 1: Sealskin float before treatment.

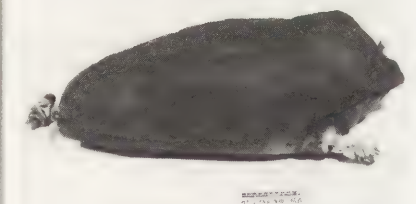


Figure 2: Sealskin float after treatment.



Figure 3: A pair of Eskimo sealskin boots. After arriving damp and distorted, one was padded and freeze-dried, the other allowed to air-dry as received.

## EXPERIMENTAL FREEZE-DRYING OF ETHNOGRAPHIC SKINS AND GUT

Barbara Wills, Andrew Calver, and Philippa Cruickshank  
Department of Conservation, The British Museum, London WC1B 3DG

## 1. INTRODUCTION

The British Museum's collections include a number of skin, hide and gut artefacts which show specific types of damage. Untanned and semi-tanned skins are particularly susceptible to low relative humidity, which dehydrates and embrittles them. Dry conditions can also result in the retention of creases in objects that have been stored in a folded condition. When in contact with water, such skins become more pliable, but on drying will return to a hard and brittle state, possibly worse than before wetting. The freeze-drying process<sup>(1)</sup> removes water from an object by freezing and subsequent removal of the ice by sublimation, thus by-passing the liquid state. This technique could therefore allow the use of aqueous conservation treatments, including the introduction of a humectant, without the damage that can be incurred by air-drying.

## 2. THE FREEZE-DRYING OF SELECTED ESKIMO ARTEFACTS

After collection and packing in a humid environment followed by prolonged transport, newly-acquired Eskimo articles have, on occasion, arrived at the British Museum in a damp condition. Such objects have usually been allowed to air-dry, which has resulted in stiffness and distortion, and the need to re-humidify to remove creases. A modern sealskin float which had been allowed to dry in this way was made pliable again by re-humidifying, re-shaping and freeze-drying.

The float (Figure 1) was sprayed with distilled water and allowed to remain damp overnight. It was then inflated<sup>(11)</sup> while supple and frozen in this expanded state at a temperature of -20°C. When frozen stiff, the stopper was removed and the float freeze-dried. After removal from the vacuum chamber it was immediately weighed. It was noted that the object's weight gradually increased, reaching a constant level after three weeks in a stable environment of 55% (Figure 2). After this time, the float was flexible enough to be inflated for exhibition purposes, but deflated for storage.

Following from the success of this treatment, it was agreed that a number of newly-collected damp Eskimo artefacts should be freeze-dried immediately on arrival from Canada, in the hope of reducing stiffening and distortion on drying. Two dog-traces, a pair of trousers, two pairs of boots and a whip were made available for the experiment. One of the dog-traces was soaked in distilled water before freeze-drying, to further plump the skin and observe the results. One boot of each pair was allowed to air-dry as a control for comparative purposes. All other objects were frozen and then placed in the vacuum chamber of the freeze-drier.

The freeze-dried dog-traces showed less distortion, and were slightly more flexible than the air-dried equivalents. The dog-trace that had been pre-soaked in water appeared plumper and paler after treatment, although some areas of the surface were very slightly friable. An air-dried strap also exhibited this slight powdering of the surface after drying. The walrus ivory toggles cracked after freeze-drying along the line that separates the primary and secondary layers of dentine.

The trousers retained their fully-padded shape after freeze-drying and remained fairly flexible.

The freeze-dried boots (Figure 3) showed a slight increase in flexibility over the air-dried examples, especially on the uppers. The fur on one of the pairs appeared thicker, because the hairs were raised at a higher angle to the skin surface. After humidification and re-shaping, the air-dried boots remained more creased than the freeze-dried ones.

## 3. FREEZE-DRYING EXPERIMENTS ON SAMPLES OF SKIN AND GUT

Six types of skin and one of gut (Figure 4) were used for the tests:

- A Seal (probably Harp, *Phoca groenlandica*), collected from N. America in 1986. It had been staked, fleshed and air-dried, but remained untanned. Condition: fairly flexible, with epidermis and hair intact.
- B Seal (probably Ringed, *Phoca foetida*), collected from N. America in 1986. Also staked, fleshed and air-dried, but with the hair removed. Untanned. Condition: stiff, epidermis intact.
- C Rawhide shield, southern Africa. At least 20 years old. Condition: hard and stiff, epidermis intact, some hair remaining.
- D 'Chamois' washleather (probably split sheepskin). Modern, oil-dressed. Condition: flexible and soft, no grain surface or hair. Discoloured, distorted and slightly stiffened due to household use.
- E 'Chamois' washleather (probably split sheepskin). Oil-dressed. Condition: As manufactured and extremely flexible, no grain surface or hair.

Ds Heat-shrunk samples of washleather 'D' above.





Figure 4: Some of the skins used in the experiments.

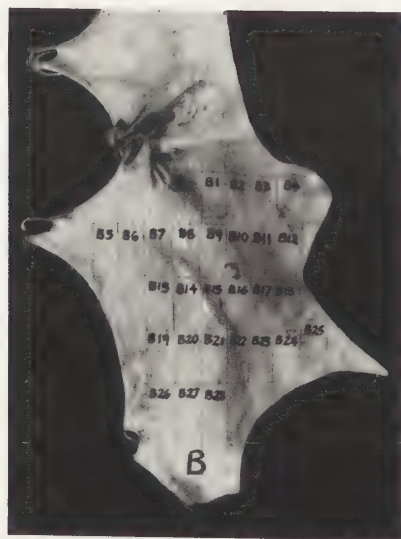


Figure 5: Seal skin B with samples drawn and marked.

**F** Deerskin collected from N. America. At least 10 years old.

Condition: slight flexibility, with epidermis and hair intact, although hair very loosely attached in places. Staked, fleshed and air-dried. Known to have been treated with 2% v/v 'Topane' (orthophenylphenol) fungicide in industrial methylated spirits, followed by 'Bavon ASAK ABP' as a dressing, 50% v/v in white spirit. This treatment had probably been carried out when the hide was first received 10 years ago.

**G** Seal gut membrane collected from Alaska prior to 1890.

Condition: flexible, 'crackly'.

Skins A and B were collected primarily for use in this project. Many Eskimo artefacts acquired by the British Museum are made of sealskin, so these pieces are ideal for experimental purposes. Shield C was chosen as an older example of rawhide which was large enough to give adequate samples.

Skins D and E were chosen as a substitute for N. American Indian 'buckskin' which is oil and smoke tanned, as it was not possible to obtain suitable quantities of true buckskin for experimental use. One new and one older washleather were chosen. A second set of samples from the older piece were heated to beyond the collagen shrinkage temperature in an attempt to demonstrate the possibility of regaining original dimensions by bulking or swelling the skin (Ds).

Skin F has been included as an example of a skin that has been treated at some time in the past with an excessive amount of dressing, a condition common among conserved skins and leathers.

Gut G was chosen because it was thought that the freeze-drying process might improve the success of current treatments of gut.<sup>(2,3,4,5,6)</sup>

The outlines of the samples were marked out on to each skin in pencil, and numbered with a waterproof ink. Photographs were then taken to record the location of each numbered sample on each skin (Figure 5). Samples were cut to a size of 25 mm by 50 mm using a sharp knife. To obtain comparative results, the long axis of each sample followed the direction of the hair follicles where possible. Skin samples Ds were placed in an oven over a two-week period and the temperature gradually raised to 100°C, after which a discernable shrinkage was noted and recorded. All samples were then placed in a humidity cabinet with conditioned silica gel at a constant relative humidity of 55%, with the exception of Gut G which was not available in time. After a week they were weighed. The thickness was measured at a marked spot at the top edge and centre of each sample using a micrometer. The size was recorded by tracing the outline with a sharp 2H pencil on to polyester drafting film.

After considering information from relevant articles on the freeze-drying of waterlogged skins and leathers and on the treatment of gut, it was decided to use two grades of polyethylene glycol (PEG)<sup>(3,4,5,7)</sup>, glycerol<sup>(8,9,10)</sup> and sorbitol<sup>(6)</sup> as the humectants for the preliminary series of experiments. Four samples from each of the skin types A, B, C, D, E, F and two samples from each of types Ds and G were used for each pre-treatment. The pre-treatments were as follows, using a separate container for each skin type.

- Immersion in 10% v/v PEG 400 in distilled water.
- Immersion in 10% w/v PEG 1500 in distilled water.
- Immersion in 10% v/v glycerol in distilled water.
- Immersion in 10% w/v sorbitol in distilled water.
- Immersion in distilled water.
- Placing in an environment of high humidity (85% RH).

After pre-treating the samples over a three day period, they were removed and the outlines traced on to the drafting film. Those soaked in distilled water alone were measured for thickness, to give an indication of the degree of swelling induced by the water.

The samples were then divided into two groups, one to be freeze-dried, and the other to air-dry. Two samples of each skin type had been kept untreated as controls at a constant relative humidity of 55%. The group to be freeze-dried was placed in a domestic freezer overnight, at a temperature of -25°C, and then transferred to the vacuum chamber of the freeze-drier. The samples remained in the chamber for ten days at a temperature of -20°C. They were weighed again immediately after removal, and then placed in a humidity chamber to condition at 55% RH for three weeks, together with the air-dried samples and controls.

The results were as follows (and are presented in tabular form as an appendix):

Sealskins (skins A and B)

**Appearance:** All sorbitol-treated samples, and freeze-dried samples of skins A and B pre-treated with PEG 1500, had a superficial white powdery deposit. Freeze-dried samples of skin B, with the exception of those pre-treated in a high RH, became markedly paler in colour, especially those pre-treated with water alone. Air-dried samples generally showed more distortion than those that were freeze-dried.



**Area:** Samples pre-treated with water decreased in area (up to -7%). Others showed a slight change (-7% to +5%).

**Thickness:** All humidified samples lost about -6%. Of the others, all freeze-dried samples increased considerably (up to +50%). Apart from the glycerol pre-treatment, other air-dried treatments resulted in minimal change or shrinkage of up to -12%.

**Flexibility:** Freeze-dried samples tended to be slightly stiffer.

#### Rawhide (skin C)

**Appearance:** All sorbitol and PEG 1500 treated samples showed a white powdery deposit. Air-dried samples were slightly distorted, which was most marked after pre-treatment with water.

**Area:** All the freeze-dried and the air-dried sorbitol samples showed minimal change (-1% to +1%). Other air-dried samples became slightly larger (up to +4%).

**Thickness:** Humidified samples lost about -4%. Of the remainder, all freeze-dried samples gained (up to +37%). With the exception of the glycerol pre-treatment, all other air-dried samples remained unchanged or contracted (up to -9%).

**Flexibility:** Little change.

#### 'Chamois' wash leathers (skins D, Ds, and E)

**Appearance:** All sorbitol and PEG 1500 treated samples had a whitish deposit on the surface. Samples pre-treated with sorbitol and allowed to air-dry showed a darkish waxy area around the cut edges. PEG 400 pre-treatments led to some bleeding of the marking ink, and a slightly clammy feel.

**Area:** Humidified samples decreased in size (up to -10%) as did air-dried water pre-treatments (up to -5%). With minor exceptions, all others gained in area (up to +12%).

**Thickness:** All humidified samples, air-dried skin E and PEG 1500 became thinner (up to -35%). Other samples gained, notably PEG 1500 and sorbitol (up to +31%).

**Flexibility:** All sorbitol and PEG 1500 pre-treatments became slightly stiffer. PEG 400, glycerol and humidified samples became more flexible.

It was interesting to note that the heat-shrunk samples (Ds), which lost an average of 12% of their original area on heating, reverted to a slightly larger size than the original after almost all aqueous immersion pre-treatments.

#### Deerskin (skin F)

**Appearance:** All freeze-dried samples had lost translucency and become much paler in colour. Those that were air-dried also tended to be slightly paler, apart from the glycerol and PEG 400 treated samples.

**Area:** With the exception of PEG 1500, all air-dried samples gained (up to +7%), all freeze-dried samples showed minimal change or were slightly smaller (up to -3%).

**Thickness:** Apart from the humidified samples, which showed little change, all pre-treatments resulted in an increase, with the air-dried samples up to +22% and the freeze-dried to +64%.

**Flexibility:** Those pre-treated with water, PEG 1500 and sorbitol became stiffer. Samples pre-treated with PEG 400 and glycerol became more flexible.

#### Seal gut membrane (gut G)

This was not fully conditioned before treatment, so the results should be approached with caution. It was impossible to measure the thickness accurately with the equipment available, because of the thinness of the material and the very slight change before and after treatment.

**Appearance:** The humidified samples became slightly stiff and crinkly. Those treated with PEG 400 were limp, especially the freeze-dried sample. The air-dried sorbitol sample had a white powdery deposit.

**Area:** All the freeze-dried samples decreased in size (up to -12%), with the exception of the PEG 1500 treated sample, which increased minimally. Air-dried samples tended to shrink less than the freeze-dried, and the PEG 400 air-dried sample became slightly larger.

**Thickness:** Freeze-dried samples of glycerol, sorbitol and high humidity pre-treatments increased in thickness; all others became thinner.

**Flexibility:** Humidified samples were stiffer. PEG 1500, 400 and sorbitol increased the flexibility, especially the freeze-dried sample of PEG 400.

#### 4. DISCUSSION OF RESULTS

##### Weight changes:

As expected, samples pre-treated with high humidity and water showed little increase in weight, with the exception of gut. The pre-treatments involving the use of humectants led to a weight gain, which was considerable with skins C, D, Ds and E (up to +65%).

Gut G showed the most remarkable change (up to +160%). However, the lack of RH conditioning of the gut before pre-treatment may have distorted this result.

Skin F was not weighed because the hair loss during treatment would invalidate the result.

##### Comparison of results due to pre-treatments:

After treatment the humidified samples of skin showed a general reduction in area and thickness, but remained constant or increased in flexibility.

Pre-treatment with water led to a slight stiffening and a considerable gain in thickness after freeze-drying.

Pre-treatment with PEG 400 encouraged the marking ink on the samples to bleed, and gave a clammy feel to the thinner samples. It tended to increase flexibility and lead to a general increase in surface area. The thickness increased with freeze-drying, and decreased with air-drying.

Both PEG 1500 and sorbitol treatments tended to leave a superficial white powdery deposit, and also lead to a slight stiffening of the samples. Sample thickness increased with freeze-drying and decreased with air-drying.

The glycerol pre-treatment increased the thickness of both air and freeze-dried samples, although this was more pronounced with the latter, and produced increased flexibility throughout.

##### Comparison of the freeze-drying and air-drying process:

The freeze-drying process tended to remove creases and show less distortion on drying. It also increased the sample thickness considerably. On the grain side of sealskin B a strange greyish surface developed, which appeared to be related to the expansion of part of the epidermal layer. There was also a general tendency for the skins (not the gut) to become paler in colour on the flesh side. This was probably due to the change in skin structure; the collagen fibres having swollen while immersed in an aqueous medium and that open structure having been retained after treatment. This would also account for the more raised hair follicles noticed earlier on one of each pair of Eskimo boots. Air-dried skins (apart from those pre-treated with glycerol) tended to become thinner after treatment, and retained more of the original creases. Soaking in water followed by air-drying did lead to considerable distortion in some samples.

#### 5. CONCLUSION

The results showed that there are clear differences produced by the method of drying the skins. The benefits of the freeze-dried samples over the air-dried ones, after similar aqueous pre-treatments, included the removal of creases and a reduction in distortion on drying. However, the swelling apparent in skins after the freeze-drying process, and colour changes noted in some cases (notably in sealskins A and B), may sometimes be unacceptable.

The swelling of the skin produced by aqueous pre-treatments, and retained by the freeze-drying process, would probably be most acceptable in the treatment of shrunken and distorted skins. Since it was only possible to obtain relatively new skins in good condition for the experiments, some samples of D were heat-shrunk (Ds) to represent this type of skin. The experiments showed that nearly all of these Ds samples returned to their original size, or slightly larger, using aqueous pre-treatments regardless of the drying method used.

An increase in flexibility is only generally needed when an object is in danger because it is very hard and brittle. The skins used in these experiments were all adequately flexible for their type, and so no increase in flexibility was required. However, similar types of skin in a more deteriorated, brittle state might benefit from an increase in flexibility. Changes in the flexibility of the skins seem to be more closely related to the type of pre-treatment than to the drying process.

The benefits of freeze-drying over air-drying gut after aqueous pre-treatments may include an increase in flexibility with some humectants, though it is debateable how flexible it is desirable for the gut to be. The gut used in these experiments was in a fairly good condition and some of the pre-treatments involving the use of humectants made the gut too



limp. However, the freeze-dried samples tended to shrink slightly more on drying than the air-dried ones. This may prove unacceptable.

Aqueous treatments are sometimes the only methods of relaxing skin and gut objects sufficiently to allow them to be reshaped and any undesirable creases removed, and water is often a good cleaning medium. However, the experiments show that all aqueous treatments, whether air-dried or freeze-dried, tend to result in some dimensional changes, and sometimes also colour changes, and so these treatments should still be chosen with caution.

## 6. FURTHER RESEARCH

### Possible future investigations include:

An assessment of the moisture - regulating properties of each treatment.

The treatment of an Eskimo sealskin float by relaxing with water and air-drying, for comparison with the freeze-dried float.

Experiments using recently collected North American smoked caribou skin.

Reducing the percentage of humectants used in the treatment of skin and gut.

Pre-treatment with lubricants instead of humectants.

Investigation of the possibilities of freeze-drying composite objects without damage to associated materials.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. Hower, R.O., Freeze-drying of Laboratory specimens: a Laboratory Manual, Smithsonian Institution Press, Washington, USA, 1979.
2. Schaffer, E., "Properties and preservation of ethnographic semi-tanned leather", Studies in Conservation, **19**, (1974), 66-75.
3. Hill, L.K., "The conservation of Eskimo seal-gut kagools", The Scottish Society for Conservation and Restoration Bulletin, No. 7, (1986), 17-20.
4. Cruickshank, P., "The conservation of a group of model Eskimo boats", Museums Association Conservation Certificate Dissertation (unpublished), (1985).
5. Morrison, L., "The conservation of seal-gut parkas", The Conservator, **10**, (1986), 17-24.
6. Sturman, S., "Sorbitol treatment of leather and skin; a preliminary report", I.C.O.M. Committee for Conservation, (Proc. of the 7th Triennial Meeting, Copenhagen, 1984), 84.18.22.-25.
7. Wouters, J., "A comparative investigation of methods for consolidation of wet archaeological leather. Application of PEG-impregnation to a shoe from the 13th century", I.C.O.M. Committee for Conservation, (Proc. of the 7th Triennial Meeting, Copenhagen, 1984), 84.18.29-31.
8. David, A., "Freeze-drying of leather with glycerol", Museum Journal, **81**, (No. 2), (1981), 103-104.
9. Ganiaris, H., Keene, S., and Starling, K., "A comparison of some treatments for excavated leather", The Conservator, **6**, (1982), 12-23.
10. Starling, K., "The freeze-drying of leather pre-treated with glycerol", I.C.O.M. Committee for Conservation, (Proc. of the 7th Triennial Meeting, Copenhagen, 1984), 84.18.19-21.
11. Grant, J.H.A., "Conservation of an Inuit sealskin float; reformed around meteorological balloons", J.I.I.C.-C.G., **3**, (No. 1), (1977), 19-21.

## APPENDIX

TABLE 1: Changes in appearance between the controls and the samples after treatment, all conditioned to 55% RH

		High RH	Water	PEG 400	PEG 1500	Glycerol	Sorbitol
SURFACE APPEARANCE	AD			D-F: slight bleeding of marking ink	B: slightly darker D, E: slightly darker edges E, F: slightly clammy		A-G: white powder
				F: slightly paler	G: smoother		
	FD		A: pale B: very pale	D-F: clammy, bleeding of marking ink	B: slightly pale B-F: white powder		A-F: white powder
				G: slightly limp and smooth	F: pale		
DISTORTION	AD	B: slight	B: marked C: marked	B: slight C: slight	E: stretched		
	FD		B: slight	B: marked	B: slight		

Note: AD = Air-dried; FD = Freeze-dried

TABLE 2: Average % changes in weight, area, thickness and flexibility of the samples between measurements taken before treatment and after treatment, all samples conditioned to 55% RH.

	Skin type	AD <sup>A</sup> FD		AD <sup>B</sup> FD		AD <sup>C</sup> FD		AD <sup>D</sup> FD		AD <sup>Ds</sup> FD		AD <sup>E</sup> FD		AD <sup>F</sup> FD		AD <sup>G</sup> FD	
High RH	Weight	-1	-4	0	-1	+1	0	-2	-7	-3	-3	0	+1			+77	+78
	Area	+1	-3	+3	-2	+1	-1	-3	-4	-1	-4	-5	-10	+2	-3	-9	-12
	Thickness	-6	-6	-5	-6	-3	-5	-6	-3	-2	-4	-10	-15	-2	0	-3	-19
	Flexibility	-	+	+	+	0	0	0	0	+	+	0	0	0	0	-	-
Water	Weight	-2	-1	-3	-4	0	-2	-2	+4	-4	+1	-7	-3			+64	+98
	Area	-3	-4	-7	-2	+1	-1	0	+5	-2	+4	-5	+6	+4	-3	-6	-11
	Thickness	-9	+31	-2	+50	-8	+31	-4	+15	-2	+4	-15	+2	+2	+57	+14	+8
	Flexibility	-	-	-	-	0	0	-	0	0	+	-	+	-	-	0	0
PEG 400	Weight	+8	+9	+3	+3	+6	+6	+33	+64	+24	+56	+44	+77			+93	+160
	Area	+5	+2	+1	+1	+4	+1	+10	+11	+6	+6	+3	+1	+4	+1	+2	-2
	Thickness	-4	+15	-5	+22	-7	+16	+4	+12	+3	+6	-32	-10	+10	+25	+9	+26
	Flexibility	+	-	0	+	-	0	0	+	0	+	+	+	+	+	+	++
PEG 1500	Weight	+4	+5	0	-1	+2	+5	+34	+31	+39	+30	+36	+53			+116	+132
	Area	+2	+1	-1	-2	+4	0	+8	+11	+8	+6	-1	+3	-3	-3	-5	+1
	Thickness	+2	+11	-8	+19	-8	+21	-12	+32	-21	+23	-24	+31	+14	+22	+6	+6
	Flexibility	-	-	+	0	0	0	-	-	-	-	-	-	-	+	+	+
Glycerol	Weight	+16	+12	+9	+8	+12	-5	+47	+39	+57	+32	+65	+32			+143	+140
	Area	+5	+1	-7	-4	+4	0	+8	+8	+12	+5	+8	+4	+7	-1	-2	-4
	Thickness	+6	+30	+2	+39	+7	+37	+7	+17	+8	+17	-21	+4	+22	+38	-7	-11
	Flexibility	+	-	0	+	0	0	0	0	+	+	0	0	+	+	0	0
Sorbitol	Weight	+11	+12	+5	+6	+9	+7	+32	+37	+29	+33	+56	+57			+147	+127
	Area	+1	-2	-5	-1	0	+1	+5	+10	+3	+4	-3	+10	+2	-3	-7	-9
	Thickness	0	+40	-12	+40	-9	+32	+4	+24	+3	+25	-35	+21	+4	+64	+15	-6
	Flexibility	0	-	0	0	-	0	-	-	-	-	-	-	-	-	+	+

Note: 1. AD = Air-dried; FD = Freeze-dried.

2. For skin Ds average % changes given are between measurements taken before skin was heat-shrunk to those taken after treatment.

3. In assessment of flexibility "0" = similar flexibility to controls; "-" = less flexible than controls; "+" = more flexible than controls.

4. "Area" refers to the surface area of one side of the sample. This was calculated by cutting out the before and after samples drawn on to polyester drafting film, and weighing them separately, the difference in weight corresponding to the difference in area which was then calculated as % change.



# Working Group 4

Documentation

Documentation





## MEMBERS

J. M. Arnoult (France)  
J. Brown (U.S.A.)  
J. Bridgland (U.S.A.)  
P. Cannon-Brookes  
(England)  
O. Cortet (France)  
R. H. Freere (Australia)  
J. L. Guinand (France)  
K. B. Hendriks (Canada)  
K. Holm (Denmark)  
J. Mosk (Holland)  
J. Perkins (U.S.A.)  
J. H. Stoner (U.S.A.)  
R. A. Rushfield (U.S.A.)

## TRIENNIAL OVERVIEW

Coordinator  
A. J. Quint  
(U.S.A.)

## PROGRAMME 1985 - 1987

1. To promote documentation pertaining to conservation through interaction among the members of the working group and ICOM.
2. To encourage the exchange of information and contacts among worldwide experts on regional, national, and international levels.
3. To assess the validity of past, present, and future methods concerning conservation documentation.

## SUMMARY

At the 1984 meeting of the ICOM Committee held in Copenhagen, the working group on documentation came together to discuss the use of manual and automated information systems pertaining to artists' materials and techniques, conservation treatment records, and bibliographic and other reference materials. Since then, many scientific advances in documentation techniques have taken place and are the exciting subject of the triennial meeting of the working group in Sydney. There, advances will be discussed concerning the application of an enhanced documentation methodology and of newly developed automated conservation and bibliographic data bases and scientific instrumentation.

The need for greater accessibility to conservation documentation, including artists' and conservation materials and techniques, preventative and technical conservation treatment and research records, bibliographic repertoires, publications, reports, theses, and conferences, arose from loosely integrated efforts and desire for greater accessibility to conservation documentation by cultural and other institutions and organizations at the regional, national, and international levels. In part, these difficult and complex needs were underscored by the lack of understanding of the principles of analytical and computerized documentation, which was considered a peripheral activity. This lack of understanding led to a number of failed projects and experiments.

Today, there are regional, national, and international efforts to define those documentation needs and to standardize them. With regard to computerized information systems for documentation, control over and accountability for a large quantity and the quality of documentary information has led to improved accuracy, consolidation, and coordination of record-keeping to satisfy the demands of conservation, museum, library, and archival users. Increased demand has led to the use of on-demand, on-line capabilities that anticipate many documentation-related questions and interrelate and cross-reference information sources, in some cases, via networks. Thus, the user may find out about a particular object, or bibliographic or archival reference, in a reasonable period of time by employing the computer to integrate a variety of information sources.

The features of these new data bases include their ability for easier ready access and use with greater security and less maintenance and cost. In addition, conservation, curatorial, bibliographic, and archival documentation may be added, deleted, changed, modified, sorted, and printed as needed. Cultural institutions and other organizations can expect controlled syntax, terminology and data codes; maintenance of indexing thesauri or other vocabulary tools; establishment of standardized formats; and defined, specific files or records, data fields, data elements, and data standards. In the field, much has been done by the Getty Conservation Institute's Conservation Information Network in Marina del Rey, California, U.S.A., and by Stipple Database Services Limited near Abingdon, United Kingdom, which will be presented at Sydney.

New directions are also taking place in automating the Art and Archaeology Technical Abstracts, the biannual publication for

the literature of the conservation field. These innovations are taking place under the auspices of the Getty Conservation Institute.

In Denmark, the literature of the Conservation Department of the Danish National Museum in Brede is being documented and classified using a specialized system. The method provides an excellent means of locating conservation publications.

In the area of scientific instrumentation for documentation purposes, new non-destructive analytic methods have been developed. These diverse techniques include documentation by means of X-ray fluorescence, infrared reflectography, and photomacrography. The use of photomacrography for all aspects of conservation, including examination, sampling, treatment, and record keeping, and the high quality photographs and reproductions which result from this method, applicable to information pertaining to specimens and objects, will be discussed in this working group.

The presentations at Sydney will hold importance for documentation needs, providing a view of both the present and the future. With the merging of technology and conservation, we will see a new era in conservation, curatorial, bibliographic, and archival documentation. Thus, technology has become an important ally in this field, helping us move forward into the future. The papers at Sydney will make this direction clear.

The author wishes to express her appreciation to Janet Bridgland, Kirsten Grimstad, Renée Mandel, Marilyn Farley, Jean-Marie Arnoult, Kourosh Sehat, and the members of the documentation group, whose patience, understanding, and knowledge made this overview and the functioning of the working group possible.



## SUMMARY

## COMPUTERISING ART AND ARCHAEOLOGY TECHNICAL ABSTRACTS: PRESENT POSSIBILITIES AND FUTURE POTENTIAL

During the last few years, some very exciting changes have been underway for Art and Archaeology Technical Abstracts (AATA). AATA has been the major bibliographic publication for conservation for over thirty years, semi-annually providing references to the continuously growing body of conservation literature. Many revisions to AATA's publishing process have already occurred as a result of the 1983 agreement between the J. Paul Getty Trust and the International Institute for Conservation of Historic and Artistic Works (IIC) whereby the Trust assumed financial and operational responsibility for AATA. When an agreement to computerize AATA was finalized in early 1986, a number of new possibilities for AATA's future opened up. This paper briefly outlines AATA's history, present developments as part of the Getty Conservation Institute (GCI) Documentation Program, and some possible future directions.

Jessica S. Brown  
Managing Editor, AATA  
Getty Conservation Institute  
4503B Glencoe Avenue  
Marina del Rey, California 90292-6537  
United States of America

History

AATA is the only comprehensive, international bibliographic publication for the technical literature of art conservation. Its history closely parallels the growth of the conservation profession itself.

Abstracts of the technical literature on archaeology and the fine arts were first published as contributions to the journal, Technical Studies in the Field of Fine Arts, published from 1932-42 at the Fogg Art Museum, Harvard University, Cambridge, Massachusetts. In 1955, Abstracts of Technical Studies in Art and Archaeology 1943-52, a compilation of abstracts of the technical literature for those years, was published by Rutherford John Gettens and Bertha M. Usilton in order to bridge the gap in coverage caused by the war. Abstracts of Technical Studies was published at the Freer Gallery of Art, Washington, DC.

IIC Abstracts began publishing regularly in 1955 as part of IIC's developing publications program, providing an important complement to Studies in Conservation. Many individuals made quite notable contributions to this developing area of conservation documentation. Probably the name most often heard is that of John Gettens. His obituary in the 1974 AATA volume recognized the immensity of his contribution, stating:

"The very existence of AATA is largely due to Mr. Gettens who has been abstracting the literature dealing with the application of science and technology to art and archaeology from the time he was editor of Technical Studies."

In 1966, publication responsibility for the abstracts was assumed by the Conservation Center of the Institute of Fine Arts at New York University. IIC Abstracts was superseded by Art and Archaeology Technical Abstracts as of Volume Six, and with the sponsorship of NYU, a board of editors from the conservation and scientific professions in the U.S. was formed. The international network of volunteer abstractors and regional editors was expanded considerably after 1966. This group's commitment to the documentation of conservation is evidenced by the continually increasing body of literature covered by AATA in this period, information which could otherwise have been lost to the profession. Joyce Hill Stoner is probably the individual most closely associated with this period of continuous growth for AATA. Her personal and professional dedication from 1969-85 was acknowledged by the IIC Council on the occasion of her retirement as Managing Editor in October, 1985 with the following statement:

"The editorship of an international journal of this character, with a large number of voluntary contributions from many countries covering a wide span of technological disciplines, requires a combination of qualities to which very few could aspire. Joyce Hill Stoner's brilliant and dedicated work over the past 16 years, maintained with astounding consistency, places her in the front rank of contributors to the history of the conservation profession."

In the spring of 1984, soon after the Getty Trust involvement began, a questionnaire regarding AATA was circulated to IIC members. Response was a fairly impressive 34%. The average respondent was a museum conservator who had entered the profession through formal training, had been in the field six to ten years, and could read or speak English and an average of one other language besides his/her own. Average use of AATA varied from five times per year to twice a month.

The majority of respondents felt a cumulative index to back AATA volumes would be extremely helpful. Many also suggested an improved subject index, with better cross-referencing and

standardized keywording. Most found supplementary, special subject bibliographies useful. The overwhelming majority felt that both back and future issues of AATA should be computerized, provided this did not replace the hard copy publication.

#### Present Developments

In May of 1985, I joined the Getty Conservation Institute's Documentation Program as AATA's first full-time Managing Editor in over sixteen years. AATA has undergone a number of changes in the period since. In October-December, 1985, all operations were moved to California from the University of Delaware, Newark, where operations had been based from 1983.

In July, 1985 an extraordinary meeting of the AATA Board of Editors was convened to discuss the possibilities for a cumulative subject index and a future indexing system for all AATA volumes. From 1974-86, the British Museum, in computerizing its own reference database for conservation, had developed and provided the subject index published in AATA. Beginning with the 1986 volume, a new AATA subject index would be required. Many important studies of the subject index had been done by Mary Kay Porter as part of the Getty Trust Conservation Information Project's overall analysis of the information needs of the conservation profession. At that July meeting, several objectives of an eventual indexing system were articulated: simplicity, ease of use, logic, readability, the need to establish a set of clear principles, explicit, unambiguous use of terms, less redundancy, and a critical evaluation of the terminology used.

Because of the August, 1985 initiatives by the GCI Documentation Program to develop the online Conservation Information Network, it became clear that the objectives articulated at the July, 1985 AATA Board of Editors meeting could be achieved as part of this larger project. The initial proposal was to develop a mechanism for automated entry of regular AATA issues at the same time that all the back volumes were loaded into a database, thereby creating a mechanism for regular, current publication, as well as publication of cumulative indices, special subject bibliographies, and the out-of-print volumes. The Conservation Information Network became operational in April, 1986. The AATA current and retrospective volumes form a major contribution to the bibliographic database of the Network. (For further information on the Network, see paper by John Perkins in this section.)

Volume 22, Number 2, published in April, 1986, was the first AATA issue released after this agreement and contained three sections compiled from the bibliographic database of the Conservation Information Network. The number was published as a hybrid: the British Museum prepared the subject index, the abstracts were compiled manually and typeset as they had always been, and the periodicals directory and author and contributor indices were derived from the database. By the May, 1986 AATA Board of Editors meeting to review Volume 23, Number 1, the abstracts to be reviewed had already been entered to the bibliographic database. This number was the first entire AATA issue published from the Network, and, as such, has provided many helpful procedures for future Network-based publication projects.

The statistics for AATA show a gradual increase in the number of abstracts published over the past two years. Volume 22 included the largest number of abstracts ever published in one AATA volume (2624). Volume 23 was larger still, with 3126 abstracts, although it included an unusually large number of older citations which had been contributed to the Network by other institutional partners and which had not been abstracted previously in AATA.

The subject index published in Volume 23, Number 2 in May, 1987 was the first one produced as part of the Network project. In developing this index, further standardization and expansion of the terminology used in past indices, enhanced cross-referencing, and increased use of artists' and geographical names were incorporated as features. Essentially the index is a revised version of the highly permuted, quasi-hierarchical index developed previously for AATA by the British Museum. With over 29,000 name and subject terms, this index provided an average of nine subject reference points per abstract. While it is unlikely that AATA will adopt this type of indexing system permanently, it will be published in the second number of each volume for at least the next two years, as a new subject indexing system is being developed.



### The Future Possibilities

There have been many suggestions that AATA should publish on a regular calendar year. To address this issue, Volume 24 will be published as a single-fascicle volume in November, 1987. It is also possible that AATA will become a more frequent publication, given the ever increasing volume of material to be published and our ability, thanks to the bibliographic database, to publish the abstracts much sooner after the original publication date of the source document abstracted. In addition, we have for some time been discussing a new subject indexing system as well as an overall change in the look of AATA.

Besides enhancements to the regular AATA issues, there are also a number of special AATA publication projects envisioned in the next few years. Following completion of the Network Database Management project on the "cleanup" of the retrospective records in the AATA portion of the bibliographic database, an Author-Title Index to Volumes 11-24 will be produced, with an expected publication date sometime after January, 1988.

A prototype abstracts publication, incorporating a new look, new features, and the new subject index, is another special AATA publication which may be developed to test these improvements before major changes are actually introduced into production. Re-publication of the out-of-print AATA volumes (Volumes 1-7) is also an important project. (Only a microfilm of Volumes 6-7 is presently available.)

Another area which is currently being explored is the development of specialized subject bibliographies as separate, database-generated publications. Because the regular AATA issues have become so large, the option of providing a supplementary bibliography bound with the volume is no longer practical.

One other very high priority for AATA is release of a cumulative subject index to the volumes published since Volume 10. Although this project is viewed as an extremely important one, further consolidation of procedures and development of an indexing system will be coordinated with the Getty Art History Information Program before this index is published, probably not before 1989.

### The Network of Abstractors and Editors

Another AATA initiative, in conjunction with the Network, is further procedural documentation for the volunteer network of abstractors and editors for submitting abstracts to the database, in the data structure adopted by the Network's Content Review Board. While there will not be any significant change in procedures in the next year or so, an experiment to provide abstracts electronically is underway and will be further developed to facilitate contact among AATA abstractors, editors, and management.

While improved networking between volunteers and the AATA management should be accomplished through the Conservation Information Network and the electronic and hard-copy dissemination of new guidelines for submission, personal contact is another important objective for me. In the course of the last year, I have met many AATA abstractors in visits to their institutions or at professional meetings. I intend to continue trying to work personally with every individual who contributes to AATA. At the same time I will continue to look for ways to maintain the dedication of the volunteer network through incentives, such as access to the Conservation Information Network. Such incentives could ultimately lead to greater standardization and improvement in the comprehensiveness and quality of the abstracts.

In sum, then, there are many proposals for further AATA development in the next few years. There are probably more than have been outlined here. AATA has a legacy of thoughtful dedication by untold numbers of conservation professionals and we hope to continue to improve and expand the essential service that it provides.





## SUMMARY

New computer software and the creation of integrated museum relational data bases provide powerful new tools for both research and preventive conservation. Technology has to be matched with real data management requirements, and the manpower needed to support the software as well as to operate the system. STIPPLE, running on the IBM System/38, is being used successfully for collections management by the Tate Gallery, London, with the vast majority of operating functions able to be changed by the end users, rather than programmers.

## PREVENTIVE CONSERVATION AND INTEGRATED MUSEUM DATA BASES USING 'STIPPLE'

Peter Cannon-Brookes  
Museum Services Director  
STIPPLE Database Services Ltd., Warren Farmhouse, Thame Lane  
Culham, Nr. Abingdon, OX14 3DT, United Kingdom

Effective conservation management of museum collections requires a data management system which matches the complex pattern of inter-relationships between collections, staff and information characteristic of the real world of museum operations. Conservators, curators and collections managers, as the end users, have the responsibility for establishing the requirements demanded of the system, and their formulation will be based on professional expertise in the museum field. Thus particular care has to be taken to avoid compromising the future by accepting, often for ill-defined reasons, or none at all, restrictions imposed by technology which is inadequate for the tasks envisaged. The problem of matching technology with real requirements has, however, not been assisted by a tendency in the computer industry to focus publicity not on the well-tried systems running today but on the even more sophisticated technology 'just over the horizon'. Apart from inspiring an understandable nervousness in those thinking about investing in sophisticated technology, it also encourages delay by endowing the decision to do nothing with a certain respectability.

Clearly inadequate technology is to be eschewed, but once a satisfactory match between real requirements and tested technology has been achieved, there is little virtue in 'over-engineering' except as providing an ad hoc safety margin for future, undefined requirements. This can only be inspired guesswork and successes are consequently achieved at considerable financial cost. Nevertheless, the creation of integrated museum relational data bases - in which curatorial, conservation, collections management, administrative and other data are held in a single fully integrated data base - is now a practical reality for medium-sized museums as well as the best funded, and encourages the conservator to evolve new ways of thinking. Indeed, the minimisation of intervention increasingly sought by conservators will depend in no small measure on the success achieved in both establishing large integrated data bases and evolving effective means of manipulating the data in them.

Data management provides the means to store information within a logical framework, the means to retrieve that information by rational processes, and the means to manipulate it. All too often in the past the emphasis has been on the simple storage of information, with scant attention to either its retrieval or its manipulation. Storage of information is relatively easy, but its retrieval in any other form than that in which it was entered is appreciably more difficult. Consequently storage has been tacitly accepted by many as an end in itself, and not merely as a means to an end. For museums, that end is the efficient curating and conservation of the collections, and their research and publication. These institutional strategic objectives have to be established by curators, conservators and collections managers - the end users - rather than specialist computer experts or data management consultants from outside, so that in their dynamic partnership the museum professionals define their functional requirements, and the data managers and other specialists fashion the tools required to fulfill them.

Given the strategic objective of creating an integrated museum relational data base which can be navigated by conservators and other museum professionals in the future, what are the requirements of the museum for data management and the design criteria of such an integrated system? An effective data management system for museum collections must possess the following characteristics:

1. The integrity of the data to be managed must be respected scrupulously. All too often data is, deliberately or accidentally, modified before it is entered, and although the person responsible for those modifications may be aware of both their nature and their significance, subsequent users will not.
2. The system must be able to handle an almost infinite number of relationships, most of which cannot be defined now or, indeed, until they are actually required. With the passage of time and the growth of knowledge, new relationships will be recognised and the relative significance of pieces of information already entered will change. The system must be able to respond to demands for additional relationships and new ways of looking at the data.
3. The user of the system must be able to move with equal speed and freedom anywhere

within the data to which his security profile allows access. This means the rejection of artificial constraints imposed by traditional disciplinary divisions, such as Fine Arts and Decorative Arts or Old Masters and Contemporary Art, and by the familiar museum functional divisions, including curatorial, conservation, administration, collections management, library and archives.

4. The user of the system should be able to navigate the data base and utilise all its functions using, wherever possible, plain English (or such 'natural languages' as may be specified) with a bare minimum of codes, etc.

5. Since today's collection management is tomorrow's provenance, such data is identical in composition and must be handled in the same way. The data does not change with the passage of time, only the user's viewpoint changes, and it is both irrational and undesirable in a museum to have one data management system to handle the first and a different system for the second, with an obligation to transfer data from the first to the second sometime in the future, though this is precisely the practice of a number of museums which have adopted on a more or less ad hoc basis a variety of single function systems.

6. Similarly, today's condition reports are tomorrow's conservation history, and thus, as parts of the same growing body of information, they must be handled in the same way.

7. The system must be able to accept the vagaries of nomenclature and variant spellings characteristic of the real world. A wide variety of styles of description have been evolved over the centuries and re-description inevitably results in the distortion of data rejected above; but variant spellings, grammatical oddities, idiosyncracies of syntax, etc., are in their own right valuable sources of information. Consequently they should not be discarded and the system must provide a means of retrieving variants per se.

8. Since museums are storehouses of knowledge as well as storehouses of objects, the system must be able to handle within its integrated data base the museum's store of knowledge which provides the context in which the basic data concerning the museum's stock of specimens and the information narrowly based on them is understood. Indeed the value of the collection will to a considerable extent depend upon the closeness of the integration of the museum's data base. This is today often much better developed in the natural history collections than in art and archaeology collections, because the hierarchical nature of their taxonomy has facilitated the processes. In the world of artefacts systematic hierarchical relationships are to a great extent subordinate to intricate webs of interrelationships on different levels which demand appropriate techniques closely attuned to the nature of the information available concerning them.

9. The system must be able to start small and grow very large indeed without modification to the information already entered or to the operating system itself. This means that a data handling system capable of handling say 10,000 items must be able in due course to process 10m items without modifications or loss of performance. Economic constraints demand that storage capacity is only to be purchased as it is required, with a minimum of reserved space at any time, whilst the functional capability for the 10m or more items (including those item types not yet specified) is in position from the moment the system starts up.

10. Information does not become available in convenient fixed-size packages and thus the system must allow the entry of unlimited text at virtually any point, and that text must be fully integrated in the data base and handled consistently, with word processing facilities.

11. Variant information concerning a single item includes differing identifications, multiple attributions of authorship of artefacts and data, etc., and thus the system must be able to handle them consistently with easy identification of their sources.

12. From the moment of starting up, the data which has been added must be accessible and, within the limitations of that data, the system must be functioning from then.

13. High security is essential, with close control of each and every operator's access to any information, and precise logging of all additions, deletions and other alterations to the data base.

14. Users of the system should be able to expect consistent performance so as to be able to estimate accurately their manpower requirements for carrying out any specified functions, as well as to ensure the highest possible productivity given the data management resources made available. Consequently a deliberate decision may be taken to place a relatively low priority on those uses of the system which involve disproportionate amounts of computer power coupled with an adverse impact on all other users of that system. It is impossible to plan the museum's manpower requirements if the system periodically grinds almost to a halt while one operator, for example, undertakes a complex free text search. Thus either alternative operating strategies, such as undertaking these operations outside normal working hours, or other techniques to achieve the same results, are required.

Within the museum environment, micros, or personal computers (PCs), provide exceptionally good facilities for small-scale, narrowly based functions. However, notwithstanding the brilliant results achieved in modifying their operating systems and



writing sophisticated software packages, it must be remembered that these machines were basically designed for a single user carrying out a single function. Amongst the disadvantages of these modifications is the greatly increased cost of supporting the software - costs which reach alarming proportions if the long-term maintenance of networked PCs is contemplated. Apart from their relatively modest capacity and limited data handling functions, which necessarily restricts their use, the fundamental objection to allocating now the necessary financial and manpower resources is the danger of the data base rapidly outgrowing its system. The future in that respect is bleak because of the limited possibilities of upgrading such systems.

Given that data management is a means to an end, it is appropriate to consider the relative costs of the different elements in the process, and even with the more powerful systems the principal cost now lies in neither the computer nor the software but in the manpower required to operate them. Thus both the type of system and its operating characteristics have to be assessed in terms of the manpower required to support that system, as well as the manpower resources required to operate it for museum purposes. Apart from writing off capital expenditure, the former involves an assessment of the cost of maintaining the computer and the software used to operate it, and whilst the cost of the former has been in real terms declining sharply, the forward projections of the costs for programmers to write new software and maintain the existing are fearsome. Thus in selecting an effective and affordable data management system for museum purposes the objective, in this respect, must be the minimisation of the cost of new programming and of software maintenance. However, the second manpower cost assessment lies in using the system for museum operations. In this the ease of operation is a crucial factor ('user friendliness'), coupled with the response times of the system. The simple truth is that if the average response time is 3 seconds, three times as many operators will be required to execute the same number of transactions per hour as those required if the response time is 1 second or less. The aim should be to reduce the response time to human thinking time or less, because at that speed the operator becomes totally engaged with the operation he is carrying out and, like a familiar and well-oiled tool, the machine becomes an extension of the operator for the duration of the sequence of transactions. On the other hand, if the response time is appreciably longer than thinking time, the train of thought is liable to be broken frequently with consequent mistakes and loss of productivity. Thus the real cost of slow response times, in terms of manpower requirements, is even greater, and such a system can be an expensive luxury.

The strategic requirements of the museum demand the formation of a fully integrated relational data base which allows the operator to navigate freely through it, whilst economic considerations demand that the manpower requirements to establish any data management system and operate it shall be strictly controlled. A software package, STIPPLE, running on the IBM System/38, was originally written for the cataloguing of English 18th Century prints, but the facilities developed for this very exacting field have a much wider application, and the prototype was demonstrated at ICOM'83 in London (July 1983). Since early 1986, the Tate Gallery, London, has been using STIPPLE on a bureau basis using its parent, ERROS Computing Services Ltd. The latter's IBM System/38 is located near Abingdon, some 50 miles from London, and access is provided via a dedicated telephone line. Throughout 1986-87 the facility has been used for collections management by the Tate Gallery, and in particular for checking and accessioning the Turner Bequest as it was transferred from the Department of Prints and Drawings of the British Museum prior to the opening of the new Clore Gallery. However, the decision to use STIPPLE was based on a recognition of the advantages to be gained from integrating information systems which had previously been separate or under-developed. A powerful new planning and management tool is being created and the Tate Gallery conservation records will in due course form a major component of it.

Unique in that it fulfills all the design criteria set out above for an integrated museum relational data base, STIPPLE is capable of sub-second response times, whilst one of its most significant features is in respect of programming. The vast majority of operating functions, menus, etc., can be changed quickly and easily by the end user, as and when it is required, thereby drastically reducing the amount of programming needing to be undertaken, and as such it is a major breakthrough in computer technology. Furthermore, the thesaurus is a key element in the data management strategy and provides, within any STIPPLE data base, the mechanism for virtually unlimited cross-referencing, and this in turn reduces the need for complex free text searches. For the museum using STIPPLE the manpower overheads are substantially reduced as compared to other systems of comparable size and computing capacity, thus placing this powerful tool in the hands of museums which could never hope to allocate sufficient resources to operate a traditional data processing department. On the other hand the interrogation of an integrated relational

data base, using STIPPLE, makes available important information for the conservation of the collections, by giving, with appropriate security controls, the conservator direct access to a much wider range of information than was previously available through conventional documentation systems.

For example, both dealers and collectors tend to be creatures of habit, using the same restorers for considerable periods of time. A painting may display instability which is attributable to past treatment as well as hostile environmental conditions, but using STIPPLE it becomes a simple task to identify which other works in the collection passed through the same hands during approximately the same period, and then to check them for incipient instability of the same kind. Such an investigation can be undertaken using manual records so long as the curatorial department card indexes include records of past dealers as well as past collections, but this relatively simple example serves to illustrate the new types of data made available to conservators by using an integrated museum relational data base and STIPPLE. A further example stems from the integration of collections management records with conservation records, providing a ready means of correlating evidence of damage and longer term deterioration with specific borrowers, modes of transportation, display conditions, etc. The marshalling of such data will not in itself provide final conclusions, but it will assemble the relevant data in the form from which an inference can be drawn, or on which an hypothesis may be erected for future testing.

Creative thinking based on effective data management is a key element in preventive conservation, and the IBM System/38 operated with STIPPLE provides for the conservator an extremely powerful new tool.



SUMMARY

This paper briefly reviews and compares three systems for photomacrography: the SLR camera with bellows and auxiliary tubes and lenses; the stereomicroscope with attachable camera; and the photomacroscope, an instrument purpose-designed for the production of photomacrographs but also capable of being used as a sophisticated low power microscope for examination, sampling and restoration.

All three systems can use axial light paths for photomacrography, but the ease of focusing and specimen manipulation and the fixed working distance over a range of magnifications, makes the binocular systems the preferred choice for routine work.

Various accessories are available for specimen and microscope support. Illuminators for reflected and transmitted light methods and techniques for improving results according to specimen characteristics, are discussed.

Many factors, such as colour temperature, film type and contrast, are involved in attaining accurate colour reproduction.

Current exposure measuring systems, both automatic and manual, compensate for specimen area, special techniques (e.g. darkfield) and reciprocity failure. This frees the operator to concentrate on the specimen and makes photomacrography a routine method for documenting work in progress.

PHOTOGRAPHY WITH THE STEREOMICROSCOPE AND MACROSCOPE

Roy Freere  
Microscopy Division  
Wild Leitz (Australia) Pty. Limited  
P.O. Box 21  
NORTH RYDE NSW 2113 AUSTRALIA

Introduction

Small defects and repairs in museum objects often need to be photographed, both for record purposes and for instruction. To enable the detail to be clearly resolved, this may require the use of photomacrography, i.e. photography at low magnifications (conventionally from 1:1 to around 20:1). Photomacrographs have a high information content not only because of the additional magnification, but also because recognition capability (as opposed to resolution) goes down to micrometre size at only 10x magnification. This means that features such as hairline cracks and the onset of corrosion can be detected at an early stage.

The lower part of the macro range may be covered by conventional single lens reflex cameras (using macro lenses, bellows, extension rings, etc.). However, the operation of such combinations is complicated by problems such as restricted working distance, the need for high intensity illumination (or long exposure times) and limited depth of field. The object may also have to be transported to a studio: it is seldom possible to arrange photomacrography "in situ", in the middle of a conservation process. To change magnification or field of view requires re-focusing and adjustment of the object-to-lens distance.

<u>Depth of Field (μm) for SLR camera (A) and</u>					
<u>M400 Photomacroscope (B) *</u>					
* Data for circle of confusion diameter 30 μm					
A.	<u>Magnification</u> <u>on film</u>	<u>f4</u>	<u>f8</u>	<u>f16</u>	<u>Extension Factor</u>
	1:1	500	1100	2100	4
	2:1	200	400	800	9
	5:1	60	130	260	36
	10:1	30	60	120	121

B.	<u>Aperture closed to click stop</u>				
	1:1	14372	- with 0.5x additional lens		
	2:1	3056			
	5.1:1	425			
	10.2:1	102			
	16:1	41	- with 2.0x additional lens		
	20.5:1	25	- with 2.0x additional lens		

Table 1.

The Stereomicroscope

Since much delicate conservation is undertaken with the aid of a stereomicroscope a logical improvement is to equip the microscope with a camera outfit. This involves the use of a phototube, which will add a third outlet to the binocular viewing tube, to accept a camera. This combination allows photographs to be taken as and when required during a conservation process, without interrupting work and without moving the object. With some stereomicroscopes a graticule can be fitted to one of the eyepieces to allow focusing and format composition for photography via the binocular viewing tube: there is no need to peer through the



Fig 1: Wild M5 Apo Stereomicroscope with MPS-45/51 automatic camera for Polaroid pack film.

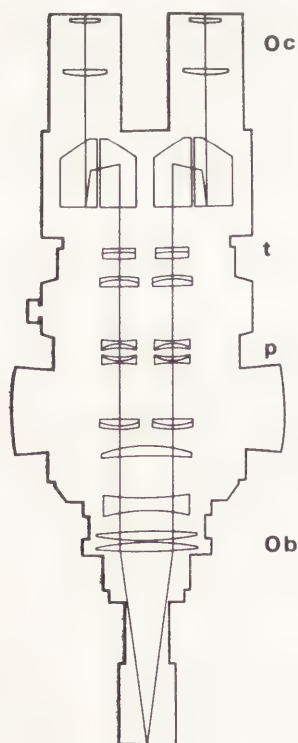


Fig 2a: M7S Stereomicroscope optics and light path with common main objective (Ob), intermediate zoom system (P) tube lenses (t), image correcting prisms and eyepieces (Oc).

camera viewfinder to observe the object, or to re-focus. The camera for use on the phototube may be an SLR with adapters and reducing lens, or a special photomicrographic camera with interchangeable formats, vibration-damped shutter and separate control unit for exposure measurement (Fig. 1.).

In the stereomicroscope, an upright, 3-dimensional image is produced by two light paths, which allow each eye to see the specimen at a slightly different angle. With the addition of the phototube this facility is retained, but a swing-in beam splitter allows light from one beam path to be directed to the camera. The camera will thus "see" the object from a slight angle. While this is not normally critical, it does mean that, particularly at higher magnifications, the image will be reduced in quality because the light path to the camera passes through the side of the common objective (CMO). This situation is overcome in certain instruments by a feature which allows the main objective to be centred below the light path to the camera (Fig. 2b).

In the stereomicroscope, as in higher power microscopes, the magnification is achieved in two stages. The intermediate or primary image is formed by the objective and is then magnified a second time by the eyepiece. Total magnification is thus the product of objective and eyepiece:

$$M_t = M_o \times M_e$$

Excessive eyepiece (or secondary) magnification will therefore only produce an image which will become more "blurred" as it is enlarged, but will contain no more details - so-called "empty magnification".

The reducing lens of the camera (which ensures that the format accepts a large portion of the field of view) has, for 35mm cameras, a factor of 0.32x. Since the phototube also contains an eyepiece, the magnification on the film is thus:

$$M_t = M_o \times M_e \times 0.32$$

Since all the resolution ("detail") is provided by the objective (the eyepiece only magnifying again the image produced by the objective) higher magnifications are best achieved by the use of supplementary objective lenses. In practice, most stereomicroscopes of the CMO type incorporate a step or zoom magnification changer, which functions as an additional objective over a certain range (e.g. 1:6). The basic ranges can be extended with additional objective lenses. A zoom component greatly facilitates composition, allowing just the right area of the object to be photographed without it being crowded into the frame of the format, or "floating" in a lot of empty space.

Most phototubes will also incorporate an iris diaphragm, which performs the same function as the f-stop in a camera lens - it allows the depth of field to be increased, as the aperture is reduced. This can assist in pulling more of the specimen into focus. However, it is important to realise that good depth of field is not the only criterion and that as the aperture is closed, the resolving power of the lens system is reduced.

The versatility of stereomicroscopes is due to the modular design

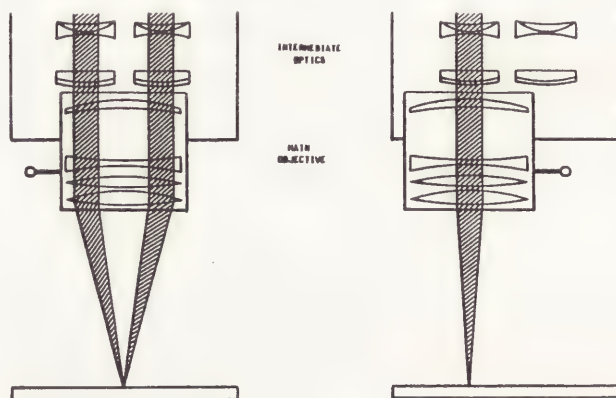


Fig 2b. Stereomicroscope in normal position (left) and in vertical beam position (right).



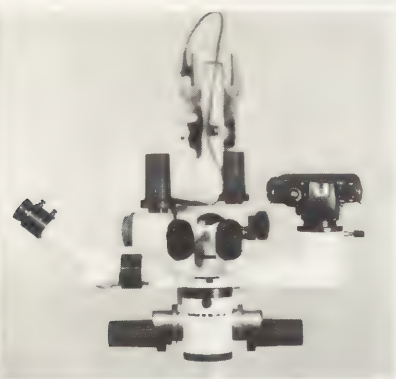


Fig 4. Stereomicroscope with camera on operating stand.

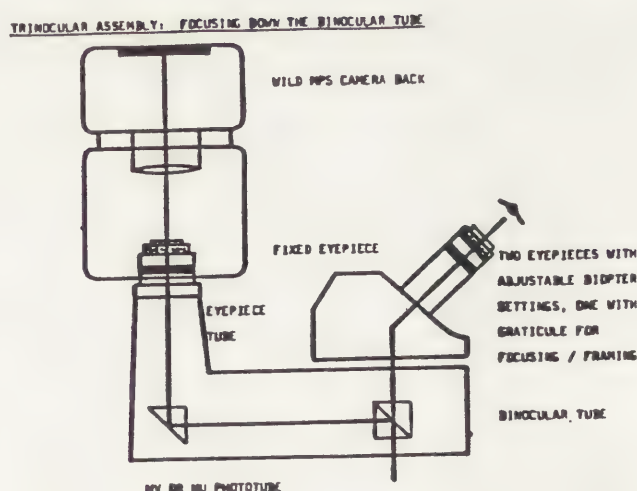


Fig.3.

concept, now followed by most manufacturers. Thus the cameras will accept a variety of formats, from 35mm film (24x36mm) to 4x5 in. (95 x 121mm). Polaroid films (e.g.  $3\frac{1}{4} \times 4\frac{1}{4}$  in: 73x95mm) are convenient for use when quick reports are needed.

Interchangeable accessories also facilitate specimen manipulation and illumination e.g. mechanical stages allow precision xy scans of areas up to 150x150mm: transmitted light bases allow bright-field and darkfield illumination: operating stands permit microscopes to be used in vertical and horizontal positions and swung over large objects (fig. 4.).

#### The Photomicroscope

In laboratories and workshops requiring a number of high quality, low power photographs a macroscope can offer distinct advantages. The Wild **M400 Photomicroscope** represents a significant step forward in photomicrography and is one of the few instruments designed specifically for this purpose, with binocular viewing and focusing facilities. A large, highly corrected objective provides a 1:5 zoom ratio. The single axial light path used for photography is split into two for binocular viewing. A high numerical aperture gives the main objective good resolving power. An adjustable beam splitter allows 100% or 50% of the light to go to the camera. This is a **direct** system, in that no eyepiece is used in the light path to the camera. This helps to maintain a high contrast image at low magnifications (fig. 5.).

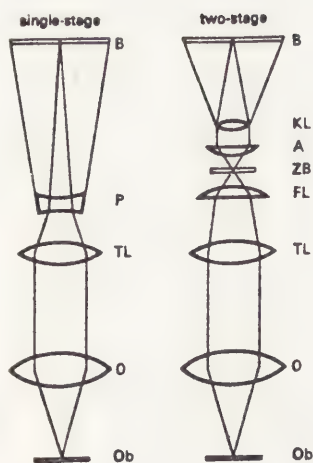


Fig 5. Single stage (left) and two stage magnification

- Ob = specimen
- O = objective
- TL = tube lens
- P = correction lens
- ZB = intermediate image
- A = eyelens (eyepiece)
- FL = field lens
- KL = camera lens
- B = film plane

Viewing eyepieces are 10x and the focus and format graticule is built-in to an eyepiece tube, with a compensating mechanism which always keeps it in the same orientation to the film plane when the eyepiece tubes are adjusted for inter-pupillary distance. This ensures accurate framing of the object.

The electro-magnetic shutter and light sensor for exposure measurement are built-in to the instrument, giving greater stability. An iris diaphragm allows depth of field variation. The binocular tube provides a higher magnification, for accuracy in focusing, and an upright image, so that specimen preparation can be carried out in much the same way as with a stereomicroscope. The parfocal 1:5 zoom range of the objective also means that very precise focusing at lower powers can be achieved by focusing on the most critical component at high power and then zooming down to cover the whole field of interest. This overcomes the tendency of the eye to accommodate and produce an apparent "in focus" position due to its greater depth of focus than the film. Long working distances allow space for specimen manipulation and a large depth of field makes it possible to work on and photograph material with considerable topographic variation (e.g. deep cavities). Like the stereomicroscopes, the macroscopes have a wide range of interchangeable mechanical components (stands, stages, etc.). The magnification range is extended by the use of additional objective lenses with bayonet mounts (Table II).

The axial light path described in the M400 and the CMO stereomicroscopes with movable main objective, is essential for accurate reproduction of polarisation effects in birefringent specimens examined between crossed polars (e.g. synthetic textile fibres, plastics, pigments). (In an off-axis system the material is not orientated at right angles to the light path and different

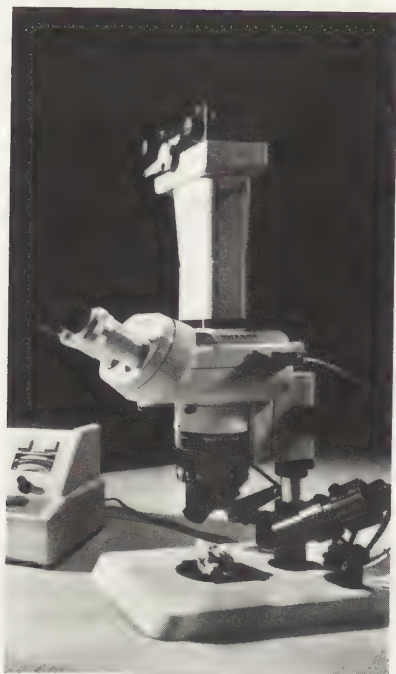


Fig 6. Photomicroscope (M400) with automatic exposure control and motorised film transport.

interference colours can be seen in each eyepiece).

### Illumination

A wide range of lamps and illuminators are available for photomicrography and need to be selected according to the type of object to be photographed.

For general purposes, **fibre optics** illuminators produce high intensity, "cold" light transmitted via flexible light guides which can be adjusted through a range of angles (e.g. very flat, glancing light to show up surface details (fig. 7a); 45° illumination of subjects under liquids). Attachable focusing lenses allow the ends of the light guides to be placed further away from the specimen. Low voltage lamps on articulated arms (either free standing or attached to the microscope) will perform a similar function, but may need extra heat filters if the specimen is heat sensitive. For larger areas, photographed at the lowest magnifications, these lamps may be more appropriate.

Relatively flat surfaces (e.g. documents) may be illuminated with a fibre optics ring light, which will also allow easy access below the objective for manipulation. Ring lights will also provide illumination of cavities (e.g. in woven fabrics; pitted metals; gramophone records; etc.) (Fig. 7c).

For flat, reflective objects (e.g. polished metal samples; integrated circuits) co-axial illumination will reveal additional detail. The coaxial illuminator for the microscope virtually converts this into a low power metallograph. A special rotating compensator, for use with this accessory, allows optimum contrast adjustment. Topography and angled illumination can produce an image full of highlights and deep shadows and a range of contrast which cannot be accommodated by the film. This can be ameliorated by the use of tubular or conical diffusers surrounding the specimen, with the lamps directed through the diffuser. (A simple diffuser can be made from an inverted white plastic "coffee machine" cup, with the base cut off - check that it will not introduce a colour-cast or that any decorative patterns will not cast shadows!) (Fig 7a and b).

Illumination from above may also cause distracting shadows and highlights which cannot be completely eliminated by using a diffuser. In such cases, transmitted light (TL) stages can be useful. If the specimen is placed on the clear glass plate of a TL stage, the shadows will "fall through" the glass and

OPTICAL DATA FOR THE M400 PHOTOMICROSCOPE

			Image scale in film plane with:		
Makrozoom objective (working distance)	Makrozoom position	Field diameter	35mm film (camera 0.32x)	6x9cm and Polaroid (0.8x)	9x12cm/4x5in (1.0x)
1.0x (102mm)	6.3x	26.6mm	2.0:1	5.0:1	6.3:1
	10 x	16.8mm	3.2:1	8.0:1	10.0:1
	20 x	8.4mm	6.4:1	16.0:1	20.0:1
	32 x	5.2mm	10.2:1	25.6:1	32.0:1
+ additional objective	6.3x	53.8mm	1.0:1	2.5:1	3.2:1
0.5x (188mm)	10 x	33.3mm	1.6:1	4.0:1	5.0:1
	20 x	16.8mm	3.2:1	8.0:1	10.0:1
	32 x	10.5mm	5.1:1	12.8:1	16.0:1
1.5x (57mm)	6.3x	17.8mm	3.0:1	7.5:1	9.5:1
	10 x	11.2mm	4.8:1	12.0:1	15.0:1
	20 x	5.6mm	9.6:1	24.0:1	30.0:1
	32 x	3.5mm	15.4:1	38.4:1	48.0:1
2.0x (39mm)	6.3x	13.3mm	4.0:1	18.1:1	12.8:1
	10 x	8.4mm	6.4:1	16.0:1	20.0:1
	20 x	4.2mm	12.8:1	32.0:1	40.0:1
	32 x	2.6mm	20.5:1	51.2:1	64.0:1

Table II.



disappear. Similarly, if a background material with a marked texture appears in focus with the specimen, it can be made less intrusive by positioning it in the base, some way below the glass plate, so that it becomes out of focus.

For transmitted light, vertical and oblique illumination will provide different degrees of contrast, while dark field will provide extreme contrast of transparent or semi-transparent material (and will also show up small particles - such as dust and fingerprints). All diffusers and filters used, as well as oblique illumination, will increase exposure times.

#### Colour Reproduction

Accurate colour reproduction is difficult to achieve and, where this is critical, it is a good plan to photograph a standard colour specimen for comparison with the final print or transparency. For good colour prints, it is usually best to produce a colour transparency and either have a print made from this (which may have a reduced contrast range) or to submit it to the processing lab as a sample for use with a colour negative of an identical area of the specimen, taken under identical conditions. Since colour reproduction will vary between types and makes of film and even between batches of the same film, it is a good plan to experiment and then to use the film which provides the best result for your material. Some professional films have tighter processing and speed rating tolerances and buying a batch of these (and storing under refrigeration) will help to maintain consistent reproduction. However, there may still be slight variations due to processing.

Colour variation may also occur if the exposure varies excessively from the optimum recommended by the manufacturers. With long exposures, the emulsion will react in a non-linear way to the amount of light available (reciprocity failure). With colour film this break down of linearity is different for each of the 3 sensitive layers, producing colour casts in the final result.

Another cause of colour shift is the use of a light source with a colour temperature ( $^{\circ}\text{K}$ ) which does not match that for which the film has been manufactured. Thus for a fibre optics light source with a colour temperature of  $3200^{\circ}\text{K}$ , the correct film would be one designed for artificial light at  $3200^{\circ}\text{K}$ , such as Ektachrome Professional EPT-5037. It is possible to use a daylight film with a suitable conversion filter (e.g. Kodachrome 25 with Kodak 80B filter), but this is not generally recommended by film manufacturers.

Sometimes macro specimens will have a very low contrast range and very pale colours. These are not appropriate subjects for colour photography and colour reproduction will almost invariably be disappointing. Better results will be obtained by using a black-and-white film of moderate speed, with a powerful developer. Where small discrete objects fall within this category, results can sometimes be made more acceptable by selecting an appropriately tinted background.

#### Exposure Determination

Most camera/microscope or macroscope outfits for photomacrography will include a built-in photocell and appropriate metering device. The M400 Photomicroscope (and some of the separate cameras for use with stereomicroscopes) are linked to a control unit for automatic exposure measurement. This allows the film speed to be set for exposure at the press of a switch, followed (for 35mm) by motor transport of the film to the next frame. In some models this can be disengaged, allowing multiple exposures on the same frame. This provides a means of increasing the apparent depth of field by dividing the metered exposure time by, say, 3; manual exposure override and slight re-focus in between three exposures on the same negative.

Where unusual material is encountered, or small, discrete objects are involved, it is advisable to take a bracket of 3 exposures (at exposure factors of e.g. 0.5, 1, 1.5) to ensure the best result. This is a much more economical solution than awaiting results, then perhaps having to hold up work, or set-up the specimen again. If the specimen covers only a small part of the field, exposure may need to be varied, for the exposure required is that which is correct for the object, not for its surroundings. Object measurement is facilitated by centrewighted and spot-measurement systems. For extreme cases, e.g. darkfield, separate meter settings may be available, which will reduce the



Fig 7. Aboriginal pigment (yellow ochre) flaking on hardwood in experimental tests for conservation of bark paintings (Magnification 12.5x)

- a) Fibre optics illumination at  $30^{\circ}$  from side.
- b) Same, with diffuser
- c) With fibre optics ring light illumination.





Fig 8. Fragment of Polynesian painted bark cloth (tapa). Magnification 6.25x)

- a) Transmitted light, bright field.
- b) Transmitted light, dark field.
- c) Combined transmitted light dark field with low angle reflected light

The film used for Figs 7 and 8 was Kodak Tech Pan, processed for high contrast. Magnifications given are as reproduced.

exposure time (this would otherwise be excessively long due to the black background, which under normal conditions would indicate a long exposure time). The electronic control units of many automatic photomicrographic cameras are also usually corrected to take account of reciprocity failure.

This paper has attempted to outline the advantages, and some of the techniques, of low power photography using stereomicroscopes and macroscopes. These instruments remove many of the problems of photography at low magnifications and help to make **photo-macrography** available as a simple routine method for documentation in all aspects of conservation.

#### Acknowledgement

It is a pleasure to acknowledge the help of the Photographic and Conservation Department of the Australian Museum in Sydney in providing specimens and film processing facilities.

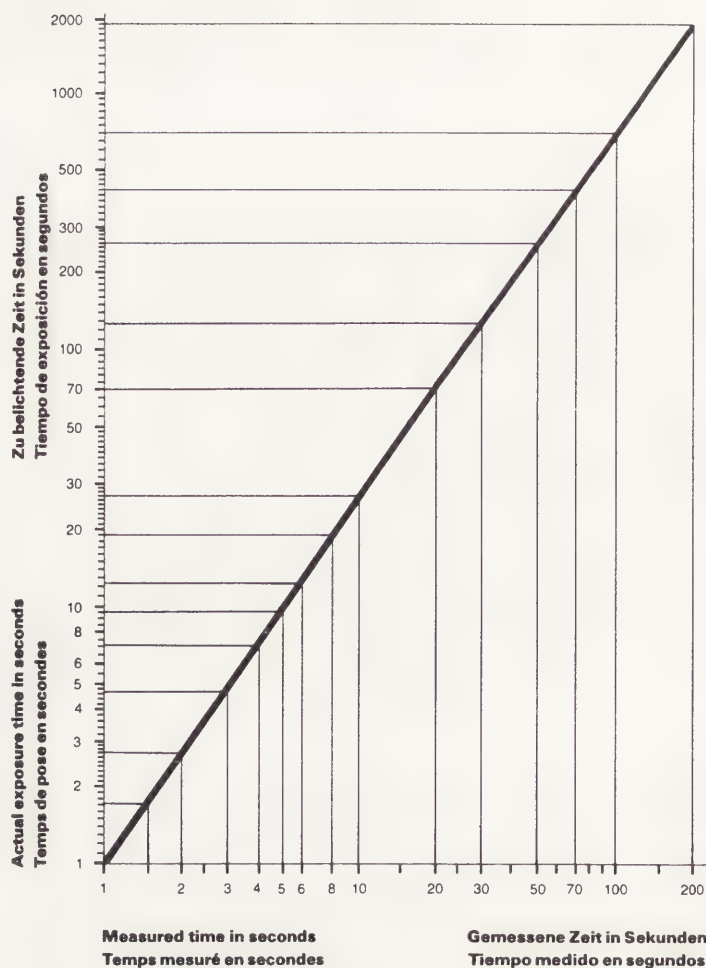


Fig 9. Typical chart for reciprocity failure correction.



A CLASSIFICATION SYSTEM FOR LITERATURE AT THE CONSERVATION DEPARTMENT OF THE  
DANISH NATIONAL MUSEUM (BREDE)

Knud E. Holm  
Chief Conservator  
National Museets  
Konserveringsanstalt 2  
Brede  
2800 Lyngby  
Denmark

The following classification system for conservation literature has been developed during the last 10-15 years by the Conservation Department of the Danish National Museum in Brede, because there was no existing system at the time that could satisfy our needs. While it has proven useful, we now wish to compare this system with others that may have been developed in the mean time.

The categories under which conservation literature is presented in Art and Archaeology Technical Abstracts (AATA) are appropriate to the purpose they serve, namely to provide a survey of the limited number of publications that appear during the half-yearly intervals between issues of AATA. However, they are not adequate for use in a growing library, where a more detailed search strategy is required to permit easy access to all of the literature.

The premise behind our proposed system is that all literature (articles, periodicals, monographs, etc.) that deals solely with one material or with a well-defined group of materials should be placed in a category according to the nature of the material. This allows specialized information on a particular material, for example, textiles, to be gathered in one place, in an orderly manner. In other words, all information on the theory, history, conservation or chemical and technical properties of a specific material or group of materials may be found in a single location.

Since many books and articles do not fit into such a specific materials structure, a second system is also required, resembling an ordinary library system, that classifies information according to individual scholarly disciplines.

1. "INNER SYSTEM" BY MATERIALS

Main Grouping

- 00 Materials Science
- 01 Metals
- 02 Inorganic non-metallic substances
- 03 Organic Materials
- 04 Paintings, Paint Materials etc.

01 Metals

- 010 Metals, General
- 011 Iron and Steel
- 012 Copper and its Alloys, Bronzes, Brass
- 013 Noble Metals, Silver, Gold, Platinum
- 014 Tin and Lead, Pewter

02 Inorganic Non-Metallic Substances

- 020 Inorganic Non-Metallic Substances, General
- 021 Rocks and Minerals
- 022 Inorganic Building Materials (incl. Mosaics)
- 023 Ceramics, Clay
- 024 Glass, Enamel

03 Organic Materials

- 030 Organic Materials, General
- 031 Bone, Antler, Tooth, Feather, etc.
- 032 Wood
- 033 Textiles
- 034 Paper and Pasteboard
- 035 Leather
- 036 Botanical and Zoological Specimens or Preparations, Fossils
- 037 Synthetic Materials
- 038 Wax, Gums, etc.
- 039 Glues and Binding Media

04 Paintings, Paint Materials Etc.

- 040 Paintings, Paint Materials etc., General
- 041 Rock Art, Cave Art
- 042 Mural Paintings
- 043 Paintings on Wood, Painted Furniture and Fixed Panels, Polychrome Sculpture.

- 044 Paintings on Canvas etc., Oil-paintings, "Easel Paintings"
- 045 Paintings in other media than Oil
- 046 Illuminated Manuscripts
- 047 Miniature Paintings (e.g. on ivory)
- 048 Gilding and Silvering in "Painters Techniques"  
(Glaze-painting and stained glass panels, look under group 024 glass)
- 049 Lacquer-work, Surface Layers with Vernish, Resins etc.

All material/categories are subdivided as follows:

- ,0 philosophy, theory, nomenclature, general or comprehensive publications on the material in question
- ,1 history, archaeology
  - a -general
  - b -individual investigations, (archaeological) finds
- ,2 materials science, chemistry, corrosion pertaining to the material in question
- ,3 technique of manufacture
- ,4 conservation of the material or group of materials
- ,5 periodicals dealing exclusively with this material or group of materials
- ,6 identification, analysis
- ,7 schools, institutes, laboratories, museums (state, governmental, municipal museums)
- ,8 societies, private collections and museums
- ,9 companies, manufacturers, dealers, wholesale catalogues

## 2. "OUTER SYSTEM" BY DISCIPLINE

### Main Grouping

- 0 General
- 1 History/Archaeology
- 2 Geography/Ethnology
- 3 Zoology/Botany/Biology
- 4 Physics/Chemistry/Mathematics/Geology/Paleontology
- 5 Technique/Art
- 6 Literature
- 7 Linguistics
- 8 Information Theory and Public Relations
- 9 Administration, Documentation
- 10 Museums and Museology
- 11 Protection, Environmental and Urban Conservation
- 12 Collection, Antique Trade
- 13 Conservation, Deterioration
- 14 Restoration
- 15 Examination Techniques
- 16 Making of Replicas, Casts, Models
- 17 Forgeries
- 18 Safety Precautions, First Aid

### Main Groups and Subgroups

#### 0 General

- 0.1 Bibliography
- 0.2
- 0.3 Encyclopaediae/Dictionaries

#### 1 History/Archaeology

- 1.1 History
  - 1.10 methods of history, critical evaluation of sources
  - 1.11 general presentations of history, history of the world
    - 1.111 miscellaneous writing with a historical content
  - 1.12 individual parts of the world, countries, regions (cultures)
  - 1.13 cultural history
  - 1.14 history of ideas, history of the sciences
  - (1.15) history of technology, see main group 5
  - (1.16) history of the crafts and of industry, see main group 5
  - (1.17) history of art, see main group 5
  - 1.18 biography
  - 1.19 aiding sciences
    - 1.191 historical iconography
    - 1.192 numismatics



- 1.193 sigillography
- 1.194 heraldry
- 1.195 writing, calligraphy

## 1.2 Prehistory and Archaeology

- 1.20 methods of archaeology
- 1.21 presentations of prehistory
- 1.22 individual cultural spheres (geographical subdivision)
- 1.23 open position not yet defined
- 1.24 open position not yet defined
- 1.25 open position not yet defined
- 1.26 excavations and finds
- 1.27 reexamination of earlier finds

## 2 Geography/Ethnology (the earth and its inhabitants)

## 3 Zoology/Botany/Biology (life)

## 4 Physics/Chemistry/Mathematics/Geology/Paleontology

### 4.1 Physics

- 4.10 physics general, physical laws, units, laboratory techniques
- 4.11 mechanical physics
- 4.12 fluid mechanics
- 4.13 mechanics of gases
- 4.14 mechanical oscillations, sound
- 4.15 light, optics
- 4.16 heat
- 4.17 electricity
- 4.18 magnetism
- 4.19 material physics, nuclear, atomic and molecule physics, solid state physics, elasticity, strength, wear, adhesion, friction

### 4.2 Chemistry

- 4.20 chemistry (including the history of chemistry)
- 4.21 general chemistry, physical chemistry
- 4.22 chemical laboratory techniques
- 4.23 analytical chemistry
- 4.24 open position not yet defined
- 4.25 open position not yet defined
- 4.26 inorganic chemistry
- 4.27 organic chemistry
- 4.28 crystallography
- 4.29 mineralogy  
(chemical technology and chemical industry, see group 5.13)

### 4.3 Mathematics

- 4.31 theory of numbers, arithmetic
- 4.32 algebra
- 4.33 geometry
- 4.34 trigonometry
- 4.35 geometry, descriptive, theory of perspective
- 4.36 analytical geometry
- 4.37 mathematical analysis
- 4.38 numerical arithmetic
- 4.39 combinatorial analysis, theory of graphs, statistics, variables, group theory, multitudes, mathematical programming

### 4.4 Geology

### 4.5 Paleontology

## 5 TECHNIQUE/ART (Material Culture)

### 5.1 Technique

- 5.10 technique in general, engineering
- 5.11 history of technology
- 5.12 mechanical technique, machining, mechanical industry
- 5.13 techno-chemistry, chemical industry, handbooks of chemical recipes for home and small industry
- 5.14 electro technics, electrical industry, electronics  
(electrochemical industry, galvanotechnics, see group 5.13)
- 5.15 crafts
  - 5.150 crafts generally (including the history of crafts)
  - 5.151 individual crafts (in alphabetical order)
- 5.16 building trades

## 5.2 Art

- 5.20 art in genral, aesthetics
- 5.21 art history, material culture
  - 5.210 art history in general, history of style, ornamentation
  - 5.211 art history, different periods, cultures etc.
  - 5.212 individual artists
- 5.22 description of objects, typology
- 5.23 ecclesiastical art
- 5.24 fine arts
  - 5.241 painting and interior decoration (including tapestries, gobelin etc.
  - 5.242 sculpture, medal art
  - 5.243 drawing and graphics, photography (as art)
- 5.25 architecture, history of architecture, description of individual buildings and building complexes
- 5.26 furniture, domestic textiles, tapestries, framework, domestic utensils, knick-knacks
- 5.27 dress, fashion, personal belongings, jewellery
- 5.28 tools and instruments, weapons, banners, saddles, harnesses
- 5.29 art handicraft, applied art, art industry, domestic industry

6. LITERATUE

Fiction and essays dealing with subjects related to museums and cultural history

7 LINGUISTICS8 INFORMATION THEORY AND PUBLIC RELATIONS

audio-visual presentations  
design and building of exhibitions

9 ADMINISTRATION/DOCUMENTATION

management, office equipment and accessories, registration systems, electronic data processing, photography etc.

10 THE MUSEUM SYSTEM

laws and acts concerning the museum system, the organization of the museum system, museology, construction of museums (see also 13.54 museum climatology), museum buildings, design of museum storage areas. individual museums, museum catalogues, museum yearbooks etc.

11 PROTECTION, ENVIRONMENTAL AND URBAN CONSERVATION

laws and acts related to protection, environment, pollution

12 COLLECTION, ANTIQUE TRADE

auction catalogues, antique yearbooks, art dealers, guidebooks for collectors.

13 CONSERVATION, DETERIORATION

- 13.1 Conservation, Its Institutional Organization
  - 13.10 sections of acts and regulations etc. concerning the conservation systems
  - 13.11 conservation, its organization in Denmark
  - 13.12 conservation, its organization in other countries and internationally
  - 13.13 conservation laboratories, institutions, workshops
  - 13.14 design of conservation laboratories etc.
  - 13.15 training of conservators, conservation schools
  - 13.16 estimation of conservation needs, reports concerning conservation requirements
- 13.2 Bibliographies of Conservation and Related Literature
- 13.3 Periodicals, Conference Preprints and Reports, Exhibitions on Conservation and Restoration
  - 13.31 periodicals and annual publications
  - 13.32 congress or conference preprints and reports (which are not exclusively devoted to a single material or to a narrow group of materials)
  - 13.33 exhibitions catalogues (from conservation/restoration exhibitions)
- 13.4 Conservation



- 13.40 conservation general, textbooks, manuals etc.
- 13.41 conservation, description of specific techniques
- 13.42 disinfection, disinfestation
  - 13.421 insecticides and fungicides
- 13.43 field conservation
  - 13.431 conservation related to natural and other disasters
- 13.44 conservation specialities which do not fit within a material grouping (the "inner system")
  - 13.441 conservation of ethnographic material
  - 13.442 conservation of film and photographic material, sound-recording on tape, audio-visual material
  - 13.443 conservation of books, etc.
  - 13.444 conservation of musical instruments
  - 13.445 conservation of art
  - 13.449 conservation of foodstuffs
- 13.45 conservation in defined geographic areas
- 13.46 conservation problems related to the transport of museum specimens
- 13.49 manufacturers and dealers of conservation and restoration equipment, catalogues etc.

#### 13.5 Deterioration, The Influence of External Factors

- 13.51 deterioration (look also under the different materials in the "inner system")
- 13.52 biological deterioration
- 13.53 harmful insects and animals generally (for literature that exclusively describes insects etc., that attack specific materials, look under relevance materials section in the "inner system")
- 13.54 museum climatology, climatology techniques, indoor climate
- 13.59 war stricken areas, natural disasters, fire

#### 14 RESTORATION

- 14.0 restoration, principles, history
- 14.1 restoration of monuments and sites
- 14.2 restoration of building

#### 15 EXAMINATION TECHNIQUES

- 15.1 substance identification
- 15.2 microscopy
- 15.3 spectrographic techniques
- 15.4 diffractometric methods
- 15.5 open position not yet defined
- 15.6 open position not yet defined
- 15.7 fluorescence analysis
- 15.8 x-ray photography
- 15.9 photogrammetry
  - for chemical analysis in more general terms look under analytical chemistry, group 4.23

#### 16 MAKING OF REPLICAS, CASTS, MODELS

#### 17 FORGERIES

#### 18 SAFETY PRECAUTIONS, FIRST AID





## SUMMARY

The computer-based Conservation Information Network aims to enhance the quality, scope and timeliness of the collection and dissemination of conservation information internationally by providing individuals and institutions with easy access to a wide variety of information relevant to the conservation of all types of cultural property. The Network is a collaborative venture between the Getty Conservation Institute and other major institutions which have significant information holdings on conservation. It currently consists of a bibliographic database, a database of materials used in conservation, a directory of suppliers and an electronic mail system, and will be broadened in future to include other related databases.

By integrating computer databases with printed material and a communications system, the Network aims to provide an international information handling system whose format and content are relevant to the needs of conservation professionals. It is designed to be comprehensive, easy to use, and affordable by all members of the profession.

The ultimate success of the Network will depend on its further geographic expansion and on the inclusion of individual as well as institutional subscribers. Although the GCI is financing a large portion of the costly initial development stages, the Network should be supported over time by its growing base of users.

## THE CONSERVATION INFORMATION NETWORK

John Perkins  
Getty Conservation Institute  
4503 Glencoe Avenue  
Marina del Rey, CA  
USA 90292-6537

Helen Jelich  
Canadian Heritage Information Network  
365 Laurier Avenue West  
Journal Tower South, 12th Floor  
Ottawa, Ontario  
Canada K1A 0M8

Raymond Lafontaine  
Canadian Conservation Institute  
1030 Innes Road  
Ottawa, Ontario  
Canada K1A 0M8

History

An important step toward improved access to conservation information through computerization was taken when the International Centre for the Study of the Conservation and the Restoration of Cultural Property (ICCROM) automated its library holdings in 1977. In June 1985, the Getty Conservation Institute (GCI) proposed the development of a bibliographic database combining ICCROM's library holdings with the material contained in Art and Archaeology Technical Abstracts (AATA). This initiative was followed by an agreement reached in April 1986, between the Getty and the National Museums of Canada, whereby the Canadian Heritage Information Network (CHIN) would provide technical support to an international Conservation Information Network and the Canadian Conservation Institute (CCI) would contribute its conservation materials database (ICARUS), developed in 1984 and implemented April 1985, as the basis for the creation of a second database within the Network. In May 1986 the International Council on Monuments and Sites (ICOMOS) agreed to contribute its bibliographic holdings on architectural conservation to the Network; in July 1986 the Conservation Analytical Laboratory of the Smithsonian Institution (CAL) also became a partner in this venture.

By the summer of 1987 the bibliographic database created from the merged holdings of these institutions contained over 100,000 citations and the materials database contained approximately 1,500 records.

Components

Three levels of service contribute to the overall design of the Network.

## 1. ONLINE COMPUTER-BASED INFORMATION DELIVERY

This principal component of the Network allows subscribers in sixty-five countries around the world direct online access to contribute or search for information in the databases.

The Network operates both as a repository of information, by storing it in a manner equivalent to an enhanced library card catalogue system, and as a publisher of information in its own right, by disseminating primary source information in the same way a journal article or a book reports scholarly activity.

Information is arranged on the computer system in a manner that allows users to find what they need easily and to transport it from the Network to their local working environments, for their own scholarly or professional needs. As users contribute their information to the Network, important additional resources are made available to a wider audience.

## 2. PRINT PUBLICATIONS AND OFFLINE DISTRIBUTION

The Network is intended to enhance rather than to replace more traditional forms of information exchange. Volume 23 of AATA is the first hard copy publication to be produced from the Network's databases and is the largest volume to date. Other information such as bibliographies, card catalogues and acquisitions lists are published in print form by various Network participants but are also available in machine-readable format.

Floppy disks containing portions of the databases are available to subscribers who have access to a microcomputer, but may lack the ability to use it online. In future, the information may also be available on CD-ROM or optical disks which will allow microcomputer access to a much larger number of records.

### 3. LOCAL DATABASE CONSTRUCTION

The Network also provides subscribers with data structures, formats, and protocols for use in constructing local databases. Complete reference manuals are available describing the database record structures and their suggested application to information management. This means that small, specialized local databases can be constructed using only some of the features of the extensive Network databases. The local databases will remain compatible with the larger system and can be merged at a later date if desired.

An indirect service to the profession is the developmental work done by the Network in the area of information technology. Gathering and disseminating information is expensive and time consuming; evaluating information about changing computer technologies, testing new products, developing applications and searching for solutions to problems are all more successful when economies of scale can be achieved. In fulfilling this research and development role, the Network can provide the critical mass necessary to conduct activities beyond the capability of smaller, scattered groups.

Figure 1 - Areas of Coverage of the bibliographic database

- A. DISCIPLINES AND AREAS OF ENDEAVOR
  - 1. Archaeological technical methods
  - 2. Architectural conservation and restoration
  - 3. Preservation of Historic Sites
  - 4. History of Technology
  - 5. Landscape and Garden Preservation
  - 6. Museology
  - 7. Training
- B. AREAS OF PRACTICE
  - 1. Analysis
  - 2. Environments and environmental control
  - 3. Examination and documentation
  - 4. Storage, display, handling, transportation
  - 5. Research
  - 6. Treatment
- C. AREAS OF STUDY, RESEARCH AND LEARNING
  - 1. Deterioration
  - 2. Education
  - 3. Ethics and philosophy
  - 4. Health hazards and toxicity
  - 5. History
  - 6. Policy, planning, legislation, administration
  - 7. Conservation Science
- D. OBJECTS
  - 1. Objects and their parts
  - 2. Collections of objects
  - 3. Materials of the following types: paper, books, and archives; photographs and audio-visual materials; paint and paintings; wood; textiles, fibers and dyes; other natural organic materials; metals and metallurgical by-products; ceramics, glass, and minerals; synthetic materials.
  - 4. Construction and technology
- E. MATERIALS AND MATERIEL USED IN CONSERVATION
 

Includes equipment, apparatus, and supplies.

  - 1. Tests, study, analysis
  - 2. Deterioration
  - 3. Application

### Information Structure

A survey conducted by the Getty Conservation Information Project in 1984 showed that regardless of specialty or location, conservators in the sample questioned, worked with extremely limited information resources and relied to a great extent on personal communication for treatment-related information (1,2). This suggests that access to information is often determined by the nature and extent of their personal libraries, their network of associates and their ability to communicate with those resources.

Therefore, the Network's computer-based system is conceived to operate in a manner that will interact with this type of manual system but that will significantly enhance the scope of available resources. Its information holdings are organized into databases which are supported by a communications system.

The databases are designed to facilitate access through an easy-to-use menu system, which uses a pre-determined structure to guide the user to information and through the use of a powerful database command language, which allows great searching capability.

#### 1. CONSERVATION BIBLIOGRAPHIC DATABASE (BCIN)

This database covers all conservation literature that relates to the principles and practice of the conservation and restoration of movable and immovable cultural property. Citations include published or unpublished monographs, serials, conference proceedings, reports, theses, audio-visual material, software, and machine-readable files.

Created from the merged holdings of the contributing institutions, BCIN includes material from documentation centers and libraries whose coverage extends beyond the conservation of cultural property. For this reason, and because it also contains material collected by individuals for their own research purposes, there may be citations that appear to have no obvious direct relevance to conservation.



Figure 2 - Example of bibliographic record

PARIS NUMBER 450  
 LITERATURE TYPE Monograph  
 BIBLIOGRAPHIC LEVEL Analytic  
 TITLE OF ANALYTIC Problems of varnishes use, appearance and possibilities of examination.  
 TITLE OF MONOGRAPH ICOM Committee for conservation.  
 4th triennial meeting  
 Venice 13-18  
 October 1975.  
 Preprints  
 Koller, Manfred;  
 Mairinger, Franz  
 AUTHOR 9 Pages  
 PAGE NUMBERS 19750000  
 DATE OF PUBLICATION English  
 LANGUAGE TEXT ICOM  
 PUBLISHER Paris  
 PUBLISHER CITY ICOM Committee for  
 MEETING NAME triennial meeting 4.  
 MEETING LOCATION Venice  
 MEETING DATE 1975 1013; 13-18  
 LOCATION OF DOCUMENT October 1975  
 ABSTRACT ICCROM  
 The observation of restorers, literary sources and analytical examination of samples are combined in the consideration of varnishes.  
 Paintings, sculptures and altar furniture are viewed with gothic and baroque.  
 Painting, history; Painting technique artistic; Painting technique material; Painting, varnish; Painting, varnish examination; Painting, varnish history; Painting, wood; Source, literary painting; Metal, varnish; Altar, altarpiece; Painting, varnish colored  
 Peinture, histoire; Peinture, technique artistique; Peinture, technique materiau; Peinture, vernis; Peinture, vernis examen; Peinture, vernis histoire; Peinture, bois; Source, littéraire peinture; Metal, vernis; Autel, retable; Peinture, vernis colore  
 From 1300 ad - to 1900 ad  
 Gottweig  
 Central Europe; Austria;  
 Niederösterreich; Klosterneuburg; Central Europe; Austria;  
 Niederösterreich Europe centrale; Autriche; Autriche (basse); Klosterneuburg; Europe centrale; Autriche; Autriche (basse)  
 ICOM 72/22/9  
 02799334  
 ICCROM

Figure 1 shows the intended scope and subject coverage of BCIN. This structure does not reflect a classification system since subject coverage is determined by the collective contributions to the database. It can be described as a merging of AATA's classification scheme with the subject areas covered by the ICCROM library. Additions have been made to this basic structure to describe the areas of activity of other contributors which were not accommodated sufficiently by either AATA or ICCROM. The inclusion or exclusion of a citation is a function not only of its subject but also its source. Certain core journals and conference proceedings which are central to the profession may be assumed to be fully covered. Material from more peripheral sources is included whenever it is of interest to the conservation profession.

Much attention has been paid to international standards for information exchange in the definition and formatting of the bibliographic database. The record format adheres to ISO 690-1975 (3) except where additional elements were added to identify and describe certain document types. In most cases these additions correspond to the UNISIST format (4) although in some cases BCIN has created a standard. Wherever possible the citations adhere to library cataloguing standards particularly as described by the Anglo-American Cataloguing Rules, 2nd edition (5). Where additional assistance was required the UNISIST Reference Manual was used (4).

Figure 2 shows of a typical BCIN record and demonstrates how the database is a bibliographic reference tool containing abstracts as well as standard bibliographic information. The location of hard copy versions of the texts cited is also indicated when it is known.

## 2. CONSERVATION MATERIALS DATABASE (MCIN)

This database contains information on materials used in conservation and is designed to allow retrieval and comparison of materials based on their technical properties and observed characteristics.

The initial structure of MCIN was derived from ICARUS, the computerized information system developed by CCI (6). Modifications were made to the ICARUS materials-related data structure when the Network's materials database was created to enable GCI to enter the results of its testing program on coatings and other products. Subsequently, CCI began adding information on pesticides and expanded the original entries on adhesives and consolidants.

There are four major categories of information in this database: adhesives, consolidants, coatings and pesticides. New categories of materials will soon be added, including pigments, solvents, backing boards, storage and display materials.

Figure 3 shows the two record types within the materials database plus the major groupings of the more than 500 separate fields of information within the record types.

Technical properties describe the material in a pure or unadulterated form, as one might receive it from the supplier. These data can be obtained from manufacturers' data sheets, from technical handbooks, from the literature, and from measurements and analyses undertaken by conservation research laboratories. Each individual material has one corresponding technical record in the database containing this information. Figure 4 shows a portion of the technical record for Acryloid B-72.

In practice, materials are often used in specific recipes mixed with other compounds and solvents. This can lead to very different characteristics than those described in the technical record for that material. Observed properties are those characteristics noted by conservators under actual conditions of use in a given application or conservation treatment. Consequently a material may have a number of observed records associated with it, each one corresponding to a different use in conservation. Figure 5 shows an example of one observed record for Acryloid B-72. Currently there are approximately 1000 technical and observed records in the materials database.

Figure 3 - Materials Database Structure

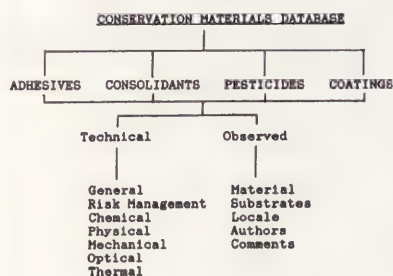




Figure 4 - Example of a technical record  
for B-72 in the materials database

MCIN NUMBER	220
USER ID	ADHV2
DATE OF BIRTH	850606
DATE OF CHANGE	870211
RECORD TYPE	TECH
BRAND NAME	ACRYLOID B-72
SYNONYM	PARALOID B-72
CATEGORY	ADHESIVES; CONSOLIDANTS; COATINGS
CLASS	ACRYLIC
FORM	SOLID
NUMBER	320
INS/DIV/OBSERVER	EDR: DOWN JL (1,2) ; GCI, DERRICK M (3, 4, 5, 6, 7)
XREF	EDR 754; EDR 912; EDR 1203; CPR 42; CPR 43; CPR 44; ARS 2380; PAR 8003 (MAIN); EDR 1522 DATA SHEET: ACRYLOID THERMOPLASTICS ACRYLIC ESTER RESINS FOR INDUSTRIAL FINISHING, ROHM & HAAS CO, APRIL 1983 (1); ARS 2380 (2) ; GCI, GPC, CG-OPERATOR, 4/86(3); GCI, THERMAL ANALYSIS LAB, MS-OPERATOR, APRIL, 1986 (4) ; MATERIALS SAFETY DATA SHEET, ACRYLOID B-72 100 % RESIN, ROHM AND HAAS, 8/85, 905259-8 (5); ENCYCLOPEDIA OF PLASTICS, POLYMERS, AND RESINS, M. ASH, CHEMICAL PUBLISHING CO., 1982 (6) ; 'PROBLEMS IN THE INVESTIGATION OF PICTURE VARNISHES', R. FELLER, ICOM, LISBON 1972 (7) ROHM & HAAS CANADA LTD ; ROHM & HAAS CO., USA A52 COATINGS (1); GLASS (1) STABLE (1); DURABLE (1); RESISTANT TO WATER (1) ACETONE=S, AMYL ACETATE=S, N-AMYL ALCOHOL=S, AROMATIC 100=S, AROMATIC 150=S, N-BUTANOL=S, N-BUTYL ACETATE=S, BUTYL CARBITOL ACETATE=S, BUTYL ALCOHOL=S, CARBON DIOXIDE=S, ACETATE=S, ME. KETONE=S, SPIRITS=1, VMA&P=1, N-PRO. ACETATE=S, TOLUENE TRICHLOROETHYLENE=S, XYLENE=S (1) 1: SLIGHT (5) VAPOR FROM HEATED PRODUCT CAN IRRITATE NOSE, THROAT AND LUNGS AND CAUSE HEADACHES, DROWSINESS, DIZZINESS AND NAUSEA. PRODUCT CAN CAUSE EYE AND SKIN IRRITATION (5) GREATER THAN 5000 MG/KG (RAT) (4) TOLUENE HAS A TERATOGENIC EFFECT IN LABORATORY ANIMALS (5). MILD ACRYLIC ODOR (5) COMBUSTIBLE, BURNS VIGOROUSLY WITH INTENSE HEAT (5) 7: C IN TOLUENE (1) STORE AT TEMPERATURES BETWEEN -18 AND 49 C (5) NORMAL ROOM VENTILATION, EYE AND SKIN PROTECTION (5) LANDFILL OR INCINERATE IN ACCORDANCE WITH LOCAL REGULATIONS (5) ETHYLMETHACRYLATE COPOLYMER (1); METHYLACRYLATE ETHYLMETHACRYLATE COPOLYMER (2); ACRYLIC 98; 100: X 98 (1); 100 % FROM REF (5) 1.15: % BY WEIGHT IN RAW RESIN (5) 35: GRAMS H2O/100 SQ IN / DAY AT 39.5 DEG C AND 100% RH (8) 0.99: G/ML (1) 7; 15.5: DEG C, VALUE 7, IN TOLUENE (1); 15.5: IN 50% TOLUENE, 70 DEG C (6) 3700; 6200: MPA.S *25C, BROOKFIELD, 50% IN TOLUENE (1) 9.3: (1) 10-11 ULTIMATE TUKON
REFERENCES	
MANUFACTURER NAME	
MANF N/A CODE	
INDUSTRIAL USES	
COMMENTS	
SOLUBILITY	
TOXICITY RATING	
SYMPTOMS	
OLD50	
TOXIC EFFECTS	
ODOR THRESHOLD	
HAZARD	
FLASH POINT	
STORAGE CONDITIONS	
HANDLING INSTRUCTNS.	
WASTE DISPOSAL	
CHEMICAL COMPOSITION	
SOLIDS CONTENT	
VOLATILES, LIQ. %	
WATER VAPOR PERMEAB.	
DENSITY	
SPECIFIC GRAVITY	
VISCOSITY	
SOLUBILITY PARAMETER	
HARDNESS	

### 3. CONSERVATION PRODUCT/SUPPLIER DIRECTORY

The Conservation Information Project survey revealed that the most frequently needed information on manufactured products used in conservation treatment concerned suppliers and availability (2). Therefore it was decided to create a database giving information on the availability of materials and suppliers internationally.

### 4. CONSERVATION INFORMATION NETWORK DATA DICTIONARY DATABASE

The record structure for all Network databases is described in the data dictionary which is available as an online database or as a printed publication. Functioning as a user's guide to the data structure, this database provides a definition of each data element or field used in any of the databases, entry format requirements, and examples of how the fields should be used.

### 5. CHIN COLLECTIONS MANAGEMENT DATA DICTIONARIES

The data dictionary databases used in CHIN's collections management system are also available. These include a Humanities Data Dictionary, which primarily describes data elements for general collections, and a Natural Sciences Data Dictionary which covers elements more closely allied to natural sciences collections. Both databases may be used to assist Network subscribers with the construction of local collections management systems.

### 6. TRAINING DATABASE

The training database is a fixed, unchanging subset of the Network databases and is used as a source of examples to illustrate training material. All material in this database also appears in the main databases.

### 7. COMMUNICATIONS SYSTEM

All subscribers have access to the ENVOY 100 electronic mail service which allows rapid and easy international communication. Subscribers may use to a wide range of features and options to compose, edit, send and answer messages.

The electronic mail system is used with the same equipment used for the Network. ENVOY also provides limited access to those who have Telex capability. While the actual electronic mail service used by the Network may change, one will be used which allows interconnections with other electronic mail services worldwide.

#### Language

English is currently the language of operation and the language of most information contained in the Network. Although the bibliographic database contains French keywords as well as titles in the original language of publication, all other contents are in English. In future, the Users Guide, Data Dictionary, and the operating software may be provided in French, if demand warrants.

While the Network databases ideally should provide information and access in many languages, this is simply not feasible at present. However, possible expansion into other languages will be investigated, to facilitate access for subscribers whose primary working language is not English.

#### System Support

CHIN operates the computer systems that house the Network databases. Since its inception in 1972, it has developed a considerable expertise in the fields of information automation and networking applications for the museum and conservation community. As well as maintaining national collections inventories to facilitate the sharing of information and the maintenance of common data standards, CHIN provides advisory services and development support for the use of new technologies.



Figure 5 - Example of a observed record for B-72 in the materials database

MCIN NUMBER 222  
USER ID -FORMS-  
DATE OF BIRTH 850606  
DATE OF CHANGE 851215  
RECORD TYPE OBS  
BRAND NAME ACRYLOID B-72  
CATGEGORY ADHESIVES;CONSOLIDANTS  
CLASS ACRYLIC  
FORM SOLID  
TYPE OF USE CONSOLIDANT  
NUMBER 320  
INS/DIV/OBSERVER FAF:STEWART C  
XREF PAR 220  
REFERENCES INFORMATION OBTAINED  
FROM FAF, STEWART C,  
QUESTIONNAIRE 340,341  
LOCAL CONSOLIDATION-PAINT  
COMPOSITE TO CANVAS  
COMMENTS SOLVENT RETENTION IS A  
SERIOUS PROBLEM HERE AND  
SETTING TIME MAY EXTEND  
TO DAYS, EVEN WEEKS.  
DARKENING AND GLOSSINESS  
INCREASE WITH THE NUMBER  
OF APPLICATIONS. NUMEROUS  
APPLICATIONS MAY BE  
REQUIRED FOR ADEQUATE  
STRENGTH. WITH A SINGLE  
APPLICATION, DARKENING  
AND GLOSS ARE IDEAL,  
STRENGTH IS AS FAR FROM  
IDEAL AS IS POSSIBLE. THE  
USE OF ACRYLOID B-72 IS  
LIMITED BECAUSE IT IS  
SOLUBLE ONLY IN  
AROMATICS. MUCH WIDER USE  
WOULD BE POSSIBLE IF  
ACRYLOID B-72 WAS SOLUBLE  
IN A NON-AROMATIC, LIKE  
HEPTANE. ALTERNATE  
RECIPE: ACRYLOID  
B-72=5-20G,  
TOLUENE=100ML.

The computer system software called the Pictorial Artifact Retrieval and Information System (PARIS) was designed specifically to accommodate the text-oriented information handling needs of all museum and conservation disciplines. PARIS is based on the BASIS database management system which runs on a Control Data Cyber 835 model computer system. Procedures have been developed to permit institutions with microcomputers to enter or retrieve records using screen-oriented data entry formats and to transmit them to and from the mainframe computer.

Equipment Required For Online Access

Any subscriber with access to a packet-switching communications network may use the Network databases online upon completion of the registration process. Packet-switching networks are available in many countries around the world and are often operated by the national Postal, Telephone and Telegraph authority (PTT). The basic equipment required is a terminal with the ability to send and receive information over telephone lines. Any of the following system configurations are acceptable:

- a) A standard ASCII terminal, and a 300 or 1200 baud modem;
- b) An IBM or compatible personal computer with a modem;
- c) An Apple Macintosh computer with a modem;
- d) Other equipment configurations approved by the Network (7).

The Network supplies a communications software package at a nominal cost for both microcomputer configurations. Potential users are given a series of tests to perform on their equipment once communication facilities are available, to ensure that all terminal and line settings are functioning correctly.

User Support and Training

All subscribers receive detailed information on the Network including a subscribers agreement, a Users Guide, and a Data Dictionary. Basic training material is provided to enable subscribers to learn to use the Network in their own working environments, at their own pace. Enhanced levels of user support include English/French telephone assistance for operational problems, live instructor training sessions held in conjunction with professional conferences, and a newsletter. Special arrangements can be made for intensive onsite training.

Network Membership

Although the Network is intended to operate in a not-for-profit manner, there are real costs that must be borne by the users. Membership by subscription is open to any individual or organization. The modest registration fee covers manuals and registration; the annual subscription is comparable to the cost of to a professional journal.

It is very difficult to predict exact usage costs as charges for use of communications networks can change quickly and rates for installation, network user accounts, and equipment costs vary from country to country. However, the cost of using the Network online is significantly lower than the rate charged by commercial database vendors. For example, a 30-minute search of the databases with approximately 25,000 transmitted characters of text, averages US\$ 20.00. (There is no charge for citations printed off-line.) This figure does not include the cost of local equipment rental or any other service charge. The user is also responsible for communications costs to the closest Network communication point.

Future Development

As the Network databases and its basic services become established, additional features and services will be developed in many areas. The materials database will be expanded to include new categories as mentioned earlier. The bibliographic database will continue to expand and a full conferencing system be added. Other databases or training courses and research in progress are being considered.

Flexibility will be maintained in order to provide a wide range of services and enhancements that will respond to the users' need for rapid access to high quality information.

## REFERENCES AND NOTES

1. Combined Questionnaire Tabulation: AIC/IIC, Volume 1, The Getty Conservation Information Project, Unpublished technical report, Spring 1984.
2. Getty Conservation Information Project Questionnaire: Selected Results, The Getty Conservation Information Project, Unpublished Technical Report, April 1984.
3. ISO Standards Handbook 1, Information Transfer, 2nd ed, ISO Geneva 1982.
4. Reference Manual for machine-readable bibliographic descriptions, second revised edition, H. Dierickx and A. Hopkinson eds., General Information Programme and Unisist, UNESCO, Paris, 1984.
5. Anglo-American Cataloguing Rules, second edition, M. Gorman and P. Winkler eds., American Library Association, Chicago, 1978.
6. A Conservation Information Retrieval System of the Canadian Conservation Institute, Ian N.M. Wainwright, in Computer Technology for Conservators: Proceedings of the 11th Annual IIC-CG Conference Workshop, IIC-CG, Halifax, 1985.
7. For information about other types of equipment, contact the Network.

## ACKNOWLEDGEMENTS

The authors would like to thank all those who have contributed to the development of the Conservation Information Network and to the preparation of this paper. Special recognition must be given to Peter Homulos, Director of the Canadian Heritage Information Network; the ICARUS development group; ICCROM, and the institutions and individuals participating in the Content Review Boards and Network Steering Committee who gave freely of their time and expertise.

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# Working Group 6

Modern and Contemporary Art

Art moderne et contemporain





## MEMBRES

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 B. MUHLETHALER (Suisse)  
 E. PORTA (Espagne)  
 A. TREMBLEY (Suisse)

## COMPTE-RENDU TRIENNAL

Coordonnateur  
 P. Cadonin  
 Picassoplatz 8  
 CH-4025 Basel  
 Switzerland

Coordonnateurs-Adjoints  
 D. Giraudy (France)  
 M. Veillon (Suisse)

Activités 1984-1987

La conférence générale de l'ICOM à Buenos Aires en 1986, nous a donné l'occasion de présenter notre groupe de travail dans l'exposition d'affiches organisée par le Comité pour la Conservation. Au lieu d'illustrer nos différentes activités, nous avons préféré montrer quelques problèmes spécifiques posés par la conservation des oeuvres d'art modernes en général: à l'aide de quelques documents photographiques pris d'un même tableau de Picasso, nous avons voulu attirer l'attention sur la fragilité insoupçonnable de certains tableaux modernes. Un texte rédigé en trois langues, complétant les informations schématiques de l'affiche traitait les arguments suivants:

- Dangers d'accidents et leurs origines
- Mutation profonde de la technique et des matériaux utilisés par l'artiste
- La matité et les problèmes qu'elle occasionne
- Nouvelle vision de l'artiste: problèmes éthiques.

Pour établir des contacts constructifs avec le CIMAM (Comité International des Musées d'Art Moderne) depuis longtemps souhaités, nous avons assisté à plusieurs séances et suivi les travaux de nos collègues de ce comité. L'intérêt pour la conservation des oeuvres modernes ainsi qu'une foule de problèmes ressentis comme urgents par les membres du CIMAM nous a valu une invitation à une table ronde organisée lors d'une réunion à Dubrovnik (mai 1987).

Orientation des Travaux

Au programme triennal (1984-1987) annoncé à Copenhague, figurait entre autres une recherche sur les phénomènes de décoloration et une étude de certaines techniques picturales modernes.

Une heureuse coïncidence nous a permis de documenter la décoloration d'un pigment rouge dans la peinture de Van Gogh et de Gauguin, étude qui permettra d'élargir la connaissance objective de l'oeuvre de ces deux artistes (Cadonin, Veillon, Mühlethaler).

Toujours sur le thème de la décoloration, deux autres contributions à notre enquête: l'une confirmant l'action de la lumière, même filtrée, sur une laque rouge (Bjarnhof, Dupont, Christensen); l'autre, sur la fragilité et les altérations chromatiques de la peinture de Mark Rothko (Cranmer).

La détérioration de la couleur blanche, couleur si importante dans l'oeuvre de Lucio Fontana, fait l'objet d'une autre contribution sur les changements de couleur (Brambilla-Barcilon).

L'autre partie de notre recherche liée davantage aux problèmes visuels, nous permet de présenter quelques cas singuliers: détection des couches inférieures de la matière picturale (Cadonin, Veillon, Trembley) et changements opérés par un artiste au cours de la création de son oeuvre (Giraudy; et Giraudy, Lahannier).

Les recherches sur la matité de la peinture et les problèmes inhérents commencent il y a plusieurs années, feront l'objet de nos travaux dans les trois années à venir et nous comptons beaucoup sur l'esprit de collaboration des collègues qui ont à coeur cet argument.





## SUMMARY

Several works of Lucio Fontana are considered here in which the dominant color of white has altered and become yellowish. Analysis reveals that this discoloration may be the result of the action of ultraviolet rays on the organic binder which has a synthetic resin base. This resin, according to documentation in the Fontana archives, is of an acrylic type.

## SOME CASES OF COLOUR ALTERATION IN WHITE PAINTINGS OF LUCIO FONTANA

P. Brambilla Barcilon  
Civiche Raccolte d'Arte  
Castello Sforzesco, Milano, Italia  
Gallone Galassi  
Istituto di Fisica del Politecnico  
P. Leonardo da Vinci, 32, 20121 Milano, Italia

Introduction

Some aspects of the technique of Lucio Fontana were considered and compared in a paper presented at the ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb, 1978, accompanied by illustrative material (1).

A collection of painting materials used by the artist were then made in connection with that paper, in hope of obtaining informations useful in the restoration of his works.

A research was carried on the artist's paintings, especially with regard to the white monochrome works realized in different materials (opaque, semi-glossy, glossy). The difference in the materials utilized becomes more evident with age: works that the artist intended to be of the same colour now present a variety of tonality of white resulting from alteration over the years. Scientific investigations were carried out, in order to obtain some indication on the possible causes of the colour change.

ANALYTICAL METHODS

The samples were first examined by optical and electron microscope. Microchemical tests were also performed.

The identification of the inorganic substance was obtained by X-ray fluorescence analysis (electron microprobe) on sample cross-sections.

The examination of organic substance was carried out by specific tests (staining tests) (^^) and microspectrofluorometric analysis on cross-sections with U.V. source ( = 366 nm).

RESULTSInorganic compounds"Concetto Spaziale 1956" - with paillettes

Sample 1 : The pigment is zinc white (ZnO). On the surface a thin layer of titanium white (TiO<sub>2</sub>), 5-10 thick, is observed.

Sample 2, 3: the pigment in these samples is zinc white.

"Concetto Spaziale 1956 - with yellow and green glasses

1A: the sample is composed by titanium white.

"Concetto Spaziale 1968" - with hole

1B: the sample is composed by extremely pure zinc oxide.

In Table 1 the X-ray fluorescence results are summarized.

Organic media

In sample 1, 2, 3, 1A a synthetic resin is present.

The binding medium in sample 1B is oil.

TABLE 1

Sample	Elements	Identified pigments
<b>"Concetto Spaziale 1956"</b>		
1-white (turned yellow) (in the centre)		
- inner layer	Zn <sup>+</sup> , Si, C, Cl, (Ti) (K), (Ca), (Fe)	zinc white
- outer layer	Ti <sup>++</sup> , S, (Zn)	titanium white
2-white (centre)	Zn <sup>++</sup> , Si, S, Cl, (K), (Ca)	zinc white
3-white with paillettes (background)	Zn <sup>+</sup> , Si, S, Cl, (K) (Ca)	zinc white
<b>"Concetto Spaziale 1956" with yellow and green glasses</b>		
1A-white	Ti <sup>+</sup> , Si, S, (Fe)	titanium white
<b>"Concetto Spaziale 1968" with hole</b>		
1B-white	Zn	zinc white (extreme ly pure zinc oxide)

CONCLUSIONS

The very thin layer observed on the surface of sample 1 consists of titanium white - a microcrystalline and fine in texture pigment - whose shiny and soft aspect is due to the binding medium used. Titanium oxide is a very stable pigment, unaffected by external and environmental agents.

Therefore, the reason why the surface white stratum is turned yellow could be associated with the ultra-violet light absorption by the synthetic resin employed as binding medium, which has different absorption properties when associated with different pigments, such as zinc white or titanium white.

An alternative interpretation is that the synthetic resin used is not exactly the same in the two paint layers.

References

1. Pinin Brambilla Barcilon, Stella Matalon "Techniques employées par le peintre Lucio Fontana et problèmes de conversation concernant son oeuvre", ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb 1978, (76/6/3)



## RESUME

L'évolution de la matière picturale et les changements chromatiques que subissent les peintures avec le temps sont des phénomènes connus, mais les cas sont rares qui nous permettent de mesurer ces altérations.

A l'occasion de l'examen de deux tableaux peints à la même époque, l'un de van Gogh, l'autre de Gauguin, on a pu documenter à l'atelier et au laboratoire la disparition d'une couleur rose sur des surfaces importantes de ces deux tableaux.

Ces observations nous portent à réviser notre connaissance de la couleur dans les oeuvres de ces deux artistes et d'autres peut-être qui auraient utilisé les mêmes matériaux.



Figure 1

Vincent van Gogh: Deux petites filles. Auvers juin 1890. Huile sur toile, 52 x 52 cm. 4

Photographie en lumière normale prise après les opérations de conservation.



Figure 2

van Gogh: Deux petites filles.

Croquis montrant l'état du tableau avant les opérations de conservation.

# DECOLORATION DANS LA COUCHE PICTURALE DE CERTAINS TABLEAUX DE VINCENT VAN GOGH ET DE PAUL GAUGUIN

Paolo Cadorin  
Picassoplatz, 8  
CH-4052 Bâle, Suisse

Monique Veillon  
Picassoplatz, 8  
CH-4052 Bâle, Suisse

Bruno Mühlethaler  
Schweizerisches Institut für Kunstwissenschaft  
CH-8024 Zürich, Suisse

## Introduction

Depuis longtemps nous sommes avertis de la précarité de certaines matières utilisées dans les oeuvres d'art moderne. Les jaunes de chrome comme ceux qu'utilisait van Gogh ont viré<sup>1</sup>, le jaunissement notoire du papier journal a provoqué des changements dans le rapport des valeurs de certains papiers collés des cubistes; de nombreuses découvertes dans la fabrication des colorants au cours de la 2e moitié du XIXe siècle ont permis la diffusion de couleurs nouvelles aux noms plus ou moins fantaisistes<sup>2</sup>, dont la stabilité s'est parfois avérée précaire par la suite<sup>3</sup>.

En général nous ne pouvons que présumer des changements de couleur qui ont pu se produire dans certaines oeuvres et il nous est difficile de mesurer ces transformations car nous manquons la plupart du temps d'éléments de référence; ceux-ci nous ont précisément été apportés avec une oeuvre de van Gogh et une autre de Gauguin, nous permettant d'approcher un peu la vérité sur la coloration originale de certains tableaux de ces deux artistes.

## Historique de l'étude

En 1967, il nous avait été possible de documenter pour la première fois la disparition d'une composante rose dans la couche picturale d'un tableau de van Gogh. En septembre de la même année, P.Cadorin avait exposé le cas oralement lors d'une réunion du Comité pour la Conservation à Bruxelles<sup>3</sup>; mais du moment qu'il s'agissait d'un cas isolé d'une portée ponctuelle, aucun mémoire écrit n'avait suivi cette présentation.

Le hasard nous a fait rencontrer récemment un phénomène analogue dans un tableau de Paul Gauguin, peint quelques mois avant celui de van Gogh; cette découverte confirme l'observation avancée sur le tableau étudié 20 ans au paravent.

## Le tableau de van Gogh

Un tableau de Vincent van Gogh de juin 1890 "Deux petites filles"<sup>4</sup> (Fig. 1) avait été apporté au Musée de Bâle en 1967 pour examen, son état de conservation posant le problème suivant:

deux bandes de toile originale peinte avaient été rabattues sur les tranches latérales du châssis et fixées avec les clous habituels comme les deux bords non-peints de la toile sur les tranches supérieure et inférieure (Fig. 2).

Le tableau avait donc été diminué de quelques cm. sur ses deux côtés.

Cependant dans toute sa partie visible, le fond du tableau montrait des tonalités bleu clair dans le haut et blanche dans le bas; lorsque les deux bandes rabattues sur la tranche étaient de couleur violacée en haut et rose en bas. Fallait-il déduire de ce fait que l'oeuvre était repeinte, ou que l'artiste avait posé d'abord un fond violacé et rose et, une fois sa toile tendue sur un châssis plus étroit, repris le fond avec des couleurs bleu-clair et blanche?

Un examen plus attentif de la couche picturale par grossissement d'une loupe binoculaire, permit d'observer à cheval sur les arêtes latérales du châssis des coups de pinceau exécutés d'un même jet, passant de la surface visible du tableau sur les bords latéraux rabattus. La continuité des rainures laissées dans la matière picturale par la brosse de l'artiste prouvait

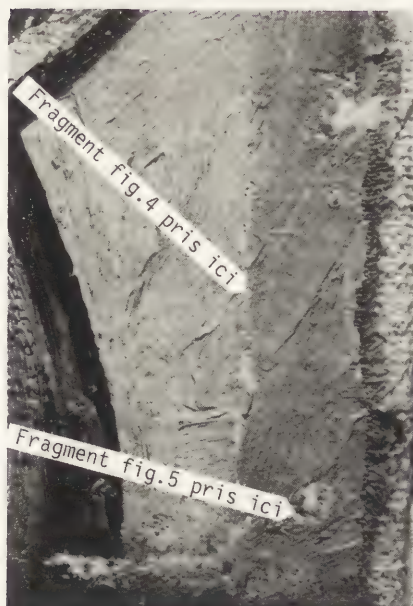


Figure 3

van Gogh: Deux petites filles.

Macrophotographie prise après que les bandes de toile peinte rabattues sur les tranches latérales du châssis aient été remises dans la continuité du plan de la surface picturale. Détail pris en X (voir ci-contre)



que l'oeuvre n'avait pas subi de transformation après qu'elle ait été tendue sur le châssis plus petit (Fig. 3). Cependant la couleur des coups de pinceau changeait invariablement, une fois passé le cap de l'arête du châssis: du bleu-clair au violacé, du blanc au rose.

L'intuition d'une décoloration de la couche picturale fut confirmée par l'examen au microscope de quelques fragments de peinture récupérés au cours de l'opération de conservation au long des cassures et de petites lacunes provoquées par l'arête du châssis et à l'emplacement des clous (Fig. 3). Les coupes de couleur exécutées par le service du Laboratoire du Landesmuseum de Zurich dirigé alors par B.Mühlethaler nous confirmèrent qu'une couleur rose, restée intacte sur le bord rabattu - à l'abri de la lumière - (Fig. 5), était totalement décolorée à la surface de la couche picturale dans la partie du tableau exposée à la lumière - cette même tonalité rose étant encore présente en dessous, et bien visible dans la coupe de couleur (Fig. 4).

L'analyse chimique révéla qu'il s'agissait d'une laque à base d'éosine, une de ces couleurs produites à partir de 1871, mise en vente auprès des marchands de Paris sous le nom de "Laque géranium" entre autres. Van Gogh, avec la prédilection qu'il exprime à cette époque pour les tons roses et violacés, utilisa cette couleur - les nombreuses commandes de "laque géranium" dans ses lettres à Théo en font foi<sup>13</sup> - mais ignorait tout de sa faible résistance à la lumière.

Au cours des recherches entamées alors, il fut possible de documenter également la présence d'éosine dans un tube de couleur ayant appartenu au Docteur Gachet, conservé dans une vitrine de la collection d'art moderne du Musée du Louvre<sup>8</sup>.

La coloration du fond du tableau de van Gogh que nous voyons blanche et bleue comportait donc à l'origine une composante rose, aujourd'hui totalement disparue. Cette constatation nous permet d'affirmer que la tonalité originale du fond était rose dans la partie inférieure et violacée dans la partie supérieure (Fig. 6).

Figure 4

Photographie et croquis d'une coupe de couleur du fragment pris au long de la cassure provoquée par l'arête de l'ancien châssis. (110 x)

Partie supérieure de la couche "rose" totalement décolorée.

Partie inférieure de la couche rose restée intacte.

Couche de préparation blanche.

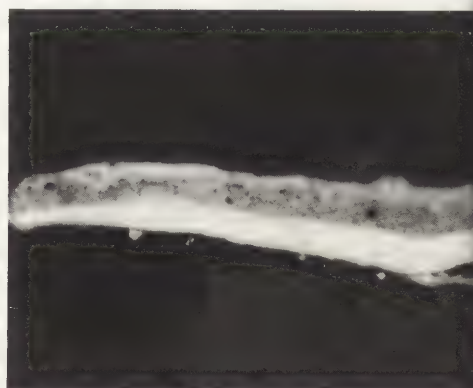
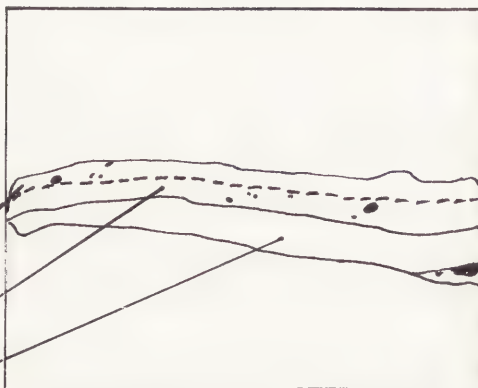


Figure 4

Figure 5

Photographie et croquis d'une coupe de couleur du fragment pris sur le bord latéral rabattu sur la tranche du châssis (donc à l'abri de la lumière). (220 X).

Couche rose restée intacte.

Couche de préparation blanche.

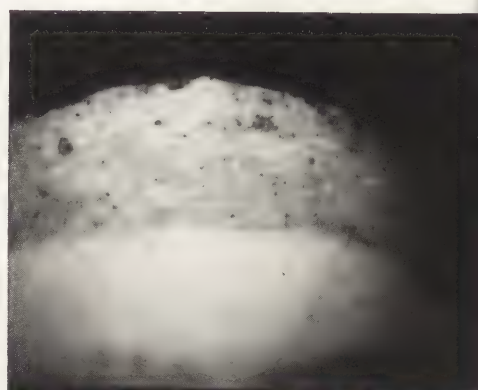




Figure 5





Figure 6

Croquis du tableau montrant la zone du fond dont la tonalité originale était rose  et la zone dont la tonalité était violacée .

D'autrepart, même si pour des raisons évidentes de respect pour l'oeuvre d'art, nous n'avons pas prélevé d'échantillons dans la région centrale de la composition, on peut se demander si le teint pâle des enfants ne proviendrait pas de la disparition d'une même composante rose.

#### Le tableau de Gauguin

A la fin de l'année 1982, un collectionneur de peintures de l'Ecole de Pont-Aven, présenta au Département de conservation et restauration du Kunstmuseum de Bâle, un tableau très semblable à celui de Paul Gauguin intitulé "Dans les Lys" 1890 et conservé dans le musée. Le collectionneur, visitant au Danemark une famille de descendants d'un peintre de l'Ecole de Pont-Aven<sup>10</sup> dans le but d'acquérir des oeuvres de l'ancêtre, avait aperçu ce tableau si semblable à celui de Gauguin, et l'avait acheté en dépit de son mauvais état de conservation.

Signé et daté en bas à droite, le tableau de Gauguin du Musée de Bâle n'a jamais été verni et n'a, à notre connaissance subi aucune restauration importante.

Le tableau ressemblant, apporté pour l'examen ne portait pas de date ni de signature. Contrairement au tableau signé, il avait subi une intervention de conservation importante: la toile avait été rentoilée à la colle de pâte et tendue sur un châssis neuf<sup>11</sup>. De plus le tableau avait été erronément verni, ce qui rendait malaisée la comparaison avec le Gauguin du Kunstmuseum.

La confrontation des deux tableaux nous fit remarquer d'abord un certain nombre de similitudes entre eux: la composition était identique: même paysage vu du même point de vue, mêmes maisons et personnages, ainsi que les lys et autres éléments du premier plan. Les mesures des deux tableaux coïncidaient parfaitement et la toile elle-même était de la même facture et sûrement de la même époque.

Quant aux différences, l'une des plus frappantes était dans la touche picturale: dans le tableau de Gauguin de la collection du Musée, une matière maigre appliquée en aplats par courts traits parallèles; dans le tableau amené à l'examen, la matière était plus grasse, appliquée en touches larges avec de nombreux empâtements. De plus, la toile était visible en plusieurs



Figure 7

Paul Gauguin: Dans les lys. 1890. Huile sur toile, 92 x 74 cm.



Figure 8


Croquis montrant la partie qui dans l'original de Gauguin est d'une tonalité gris-bleu et dans la copie est de différents tons de rose (voir zone hachurée .



Figure 9

Auteur inconnu: Copie d'après le tableau de Paul Gauguin: Dans les Lys.

endroits, ce qui pouvait suggérer d'abord l'hypothèse d'une oeuvre inachevée. Enfin, la différence la plus frappante résidait dans le fait que sur le tableau signé de Gauguin une surface assez importante du sol au premier plan comportant le chien et l'enfant était gris-bleu, alors que sur le tableau amené à l'examen, la même surface était franchement dans les tons de rose et de violet.

La supposition du départ qu'il pourrait s'agir d'une copie exécutée par un des peintres de Pont Aven d'après l'original de Gauguin, se trouvait dès lors infirmée par le fait qu'on pouvait difficilement imputer à l'élève copiant son maître une telle liberté dans la coloration d'un premier plan.

Cependant la facture et la qualité médiocre de l'oeuvre examinée nous indiquait clairement qu'il ne pouvait s'agir d'un original de Gauguin. Cette différence de coloration du premier plan, pouvait-elle dès lors provenir d'une décoloration survenue dans l'original de Gauguin ? sa copie nous donnerait alors un document précieux de la couleur d'origine ! Cette hypothèse nous avait été inspirée par le cas du tableau de van Gogh, étudié 20 ans plus tôt. La recherche de la composante rose que nous supposions disparue par l'action de la lumière fut couronnée de succès : sur le bord inférieur du tableau, dans l'étroite bande située sous le cadre à l'abri de la lumière, on put repérer des traces de couleur rose.

De minimes prélèvements de matière picturale, furent de nouveau confiés à B. Mühletheler qui nous avait déjà aidés dans la recherche engagée sur van Gogh et duquel nous publions plus bas les résultats d'analyse.

Une nouvelle fois l'analyse permit de découvrir la présence d'une laque à base d'éosine qui s'était conservée intacte dans la partie située à l'abri de la lumière sous le cadre, et qui s'était décolorée jusqu'à une certaine profondeur de la couche picturale dans la partie visible, exposée à la lumière, du tableau.

La preuve était faite que le copiste avait été fidèle et que le premier plan dans l'oeuvre de Gauguin n'était pas gris-bleu mais dans les tons de rose et de violet à l'origine.

#### Conclusion

Aujourd'hui, nous sommes certains que les deux exemples de décoloration montrés ici ne sont pas des cas isolés. Nous savons que des laques à base d'éosine ont été fabriquées à partir de 1871<sup>12</sup>.

Pour ne parler que de van Gogh, quelques remarques sur le document précieux que représente sa correspondance peuvent suggérer l'étendue du problème :

- parmi les commandes de couleurs qu'il adresse à son frère, de septembre 1888 à avril 1890, Vincent ne demande pas moins de 26 tubes de Laque géranium<sup>13</sup>.

- Le très grand nombre de mentions et la richesse des nuances qu'il trouve pour décrire des tons de "violet", "violacé", "lilas", "lilas pâle", "lilas tendre", "lilas rompu", "rose", "lilas uni, gris ou rose", "jaune tourne au rose", "rose-vert", "violet-rose"<sup>6</sup> etc... au cours de la seule époque de Saint-Rémy dont nous ne connaissons souvent que la tonalité claire et bleutée.

- Les descriptions chromatiques de ses tableaux, si précises pour certains éléments (preuve de leur fidélité), et si peu ressemblantes pour d'autres plages de couleurs : il écrit du "Ravin" : "...c'est tout violet"<sup>14</sup>, alors que l'oeuvre ne porte plus guère trace de cette couleur aujourd'hui ; ou du "Portrait du Docteur Gachet" : "...et une plante de digitale à fleurs pourpres"<sup>15</sup>, alors que celles-ci sont bleues aujourd'hui avec quelques rares accents violacés seulement.

Une recherche étendue s'impose, afin de déterminer dans quelle mesure notre vision de l'oeuvre de van Gogh et de l'art de



toute cette époque est<sup>16</sup> trahie par des changements chromatiques de la matière picturale

Avec l'aide des hommes de science, qui sont en train d'étudier les différentes méthodes d'analyse non-destructive applicables à notre recherche, nous espérons parvenir à trouver le moyen de repérer les traces restantes d'une couleur pratiquement disparue à la surface mais toujours présente dans la profondeur de la couche picturale.

Il est évident que la collaboration avec les historiens d'art nous apportera des indications précieuses pour cette recherche.

TECHNICAL EXAMINATION OF A PAINTING BY VINCENT VAN GOGH: "DEUX PETITES FILLES" June 1890. Oil on canvas, 52 by 52 cm, F.784 (Hyp.774), private collection.

This painting was remounted on a somewhat smaller cradle whereby the painted canvas became bent around the edges of the cradle. This portion of the canvas from then on remained protected from the light, and has preserved the original pink and violet colours. The light-exposed face of the canvas by now shows white in accordance with the pink areas at the edge, and blue where it should be violet, respectively. Hence fading of a fugitive red pigment is suspected.

Microscopic, microchemical and solubility tests could be performed on a few samples taken from the bent rim of the painted canvas. Upon addition of alcoholic potassium hydroxyd or dimethyl formamid a green-yellow fluorescence appeared under incident light, by transmitted light the solution appears crimson-red. When acidified the solution turns yellow, whereby the oily medium coagulates into a deep orange yellow precipitate. Upon addition of alcoholic potassium hydroxyde the former condition is restored. Upon drying of the test solution tiny hairlike crystals of cherry-red colour appeared. In incident light they showed a metallic lustre; in UV-light they showed a bright cherry-red fluorescence.

Comparative tests with a number of Eosin lakes prepared according to bibliographic sources showed principally the same behaviour.

Based on this we were inclined to admit that in the painting in question a fugitive Eosin-type lake had been used. As to its commercial designation it remains open whether it should be named "geranium lake" or "scarlet lake" or what so ever.

TECHNICAL EXAMINATION OF A PAINTING BY PAUL GAUGUIN: "DANS LES LYS" 1889. Oil on canvas, 92,5 by 73,5 cm, Basel Kunstmuseum.

Upon removal of the frame the narrow zone along the bottom edge showed traces of a pink colour. This was in contrast to the blue colour of the adjacent unprotected area. This observation rose the question whether this phenomenon was possibly due to fading of a fugitive red pigment; the initial colour being a pink shade obtained upon mixing together a more permanent blue pigment with a fugitive red lake of some kind.

Procedure: Testing possibilities being limited by number and size of samples, allowed but for a preliminary study of the case. Three samples of the "pink" zone, each measuring 0,5 by 0,5 mm only, were to be compared with one sample from the "blue" area. They were subject to microscopic, microchemical and solubility comparative testing, as was done with identified reference material.

Microscope: Leitz-Wild M10 "Orthoplan"; - with Ultropak incident-light illuminator (dark field illuminator); - Ultropak objektives with annular condensers 6,5, 11, 32 x, - 200 Watt high-pressure mercury lamp appropriately filtered; - automatic camera "Orthomat"; - Film Kodak ASA 50 Ektachrome, tungsten EPY 135-36.

Micrographs<sup>17</sup>: a (70x) shows sample taken from "pink" (light-protected) zone before being embedded in Technovit 4004a acrylic resin. White matrix is lead white + zinc white; irregular

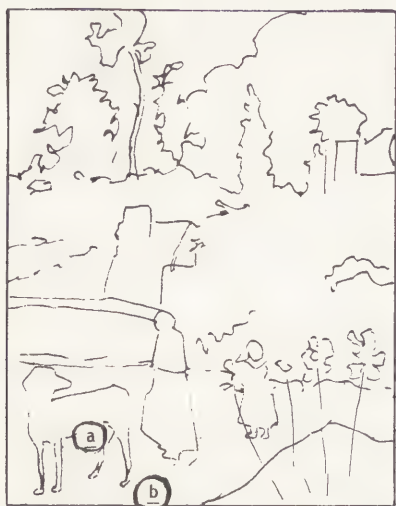


Figure 10

Croquis montrant les endroits des prélèvements a et b pour les coupes de couleurs A et B

distribution of blue particles of ferro ferricyanide pigment, green chromhydrat pigment, yellow lead chromate and a red pigment still preserved at the surface of the paint layer. Micrograph b (70x) shows a sample taken from the "blue" area (at the left of the dog's posterior leg) where the "pink" colour evidently has gone at least from the surface. However, a hue of "pink" is still recognizable at the left lower edge as well as in the right upper zone of the sample. Yet, the "red" pigment grains scattered in these two positions were identified as being madder lake.

Sample a when observed under UV-illumination distinctly showed orange-reddish fluorescence where the red pigments appear. Sample b on the contrary exhibits but a weak hue of fluorescence nearly overruled by the whitish fluorescence due to the white matrix of the paint.

Cross sections: micrograph A refers to sample a taken from the light-protected edge of the canvas and shows a nearly uniformly occurring pinkish tint of the matrix; this tint has gone in cross section B from sample b taken from the light-exposed area of the canvas. Micrograph B gives evidence of the disappearance of the red lake from the top layer of the paint; the lower zone still preserves some of the coarser particles of the fugitive red lake pigment. Its scarlet-orange shade is clearly distinguishable from the few dark red particles of madder lake.

It was also observed that the presence of Ultramarine is not to be excluded. Certain prove would require more sampling.

Final conclusion as to the precise nature of the suspected fugitive red lake pigment, should not be drawn at this state of affairs. A preliminary survey of bibliographic sources made by now reveals that by 1889 some twenty types of hydrophthaline-based colouring matters existed already (Eosins, Erythrosins, Phloxin, Rose bengale). However, based on the total of observation made, the presence of an Eosin-type lake, eg. introduced under the term "Geranium lake" should be strongly considered. The presence of a red-lead based lake - vermillionette - can be excluded. Remains open also the question whether the presence of the two red pigments is due to the intention of the artist or the colour maker.

#### NOTES

1. H. Kühn, "Farbmaterialien Pigmente und Bindemittel," in Reclams Handbuch der Künstlerischen Techniken 1. (Stuttgart: Philipp Reclam jun., 1984) p. 28.
2. Ibid., p.17.
3. Réunion du Comité de l'ICOM pour la Conservation, Bruxelles 6-13 Sept. 1967.
4. Vincent van Gogh "Deux petites filles" Auvers 1890. Huile sur toile, 51,5 X 46,5 cm. La Faille N° 784, Hypérion N° 774. N.B. Les bandes latérales de toile peinte ayant été "récupérées", c'est-à-dire remises dans la continuité du plan de la surface picturale, les dimensions du tableau sont aujourd'hui de 52 x 52 cm.
5. Voir le chapitre ci-dessous: "TECHNICAL EXAMINATION ..." les résultats des recherches de B. Mühlethaler.
6. Correspondance complète de Vincent van Gogh (Paris: Gallimard/Grasset 1960): particulièrement les lettres de l'époque de Saint-Rémy (3 mai 1889-16 mai 1890) et d'Auvers-sur-Oise (20 mai - 29 juillet 1890).
7. En 1967 nous avons prié Madame H. Adhémar, Conservateur du Musée du Jeu de Paume à Paris, de faire analyser les couleurs des tubes et de la palette ayant appartenu au Dr. Gachet, conservés dans une vitrine du Musée. Les résultats de ces analyses faites alors par les services du Laboratoire des Musées de France et sous la direction de Madame S. Delbourgo, avaient indiqué la présence d'éosine.
8. Pour peindre le portrait de Mademoiselle Gachet au piano, van Gogh avait, lors de la deuxième séance, utilisé la palette du Docteur Gachet. v.: Gachet, P. "Van Gogh à Auvers, histoire d'un tableau". Paris: Les Beaux-Arts, 1953.
9. Paul Gauguin "Dans les Lys" (autrefois nommé "Paysage breton,



chien et enfants") 1889. Signé et daté en bas à droite; huile sur toile, 92,5 x 73,5 cm, tableau déposé par la fondation Staechelin au Kunstmuseum de Bâle depuis 1947. Le tableau amené pour examen: même sujet, huile sur toile, 94 x 73 cm, ne porte ni date ni signature.

10. Gauguin avait épousé en 1873 la danoise Mette Gad; c'est par elle que des peintres danois découvrirent Gauguin et l'art français. v. Petit Larousse de la Peinture, sous la direction de Michel Laclotte (Paris: 1979) p.116.

11. La toile avait été achetée sans châssis; avant la restauration la couche picturale montrait de nombreux écailllements. (témoignage oral du collectionneur).

12. R. Gettens, and G.L. Stout, Painting Materials (New York: Dover, 1966) p. 114.

13. V. van Gogh, Correspondance complète (Paris: Gallimard/Grasset 1960): à plusieurs reprises, dans les années 1889 et 1890, Vincent commande à son frère de la laque géranium: Arles, septembre 1888: "6 tubes moyens" (tome III/p. 216); Arles, octobre 1888: "10 tubes moyens" (III/p. 241); Arles, avril 1889: "2 tubes moyens" (III/p. 318), le même mois: "6 petits tubes" (III/p. 320). Puis de Saint-Rémy, en septembre 1889, il commande "un grand tube laque ordinaire" (III/p. 376); alors que le 29 avril 1890 toujours de Saint-Rémy il revient à la laque géranium, précisant cette fois: "Puis (mais chez Tasset) 2 Laque géranium, tubes moyen format." (III/p.445).

14. Le Ravin (Les Peiroulets). Huile sur toile, 73 x 92 cm. La Faille N° 661, Hypérion N° 670. Otterlo, Musée Kröller-Müller. Correspondance (op.Cit) III/p.395 lettre 610.

15. Portrait du Docteur Gachet. Huile sur toile, 66 x 57 cm. La Faille N° 753, Hypérion N° 752. New York, prop. Kramarsky Trust Fund. Correspondance (op.cit) III/p.463; lettre 638.

16. Marc Havel, dans son livre La technique du tableau (Paris, Dessain et Tolra, 1974) p. 48 cite une publication parue en 1883 d'un petit livre intitulé "Action de la lumière du jour et de la lumière électrique sur les couleurs employées en teinture et en peinture à l'eau et à l'huile", dans lequel l'auteur M.Decaux, directeur des Manufactures Nationales des Gobelins et de Beauvais fait l'analyse de 60 couleurs d'une grande maison de Paris.

17. A cause du faible contraste des diapositives en couleurs, on a préféré montrer des croquis pour illustrer ce texte.

#### BIBLIOGRAPHIE SOMMAIRE

Gachet, P. Van Gogh à Auvers, histoire d'un tableau. Paris: Les Beaux-Arts, 1953.

Gettens, R.J.; and Stout, G.L. Painting Materials, corrected republication. New York: Dover 1966.

Havel, M. La Technique du Tableau. Paris: Dessain et Tolra, 1974.

Kühn, H. "Farbmaterialien und Bindemittel." In Reclams Handbuch der künstlerischen Techniken, Bd. 1. Stuttgart: Reclam, 1984.

La Faille, J.B. de L'oeuvre de Vincent van Gogh: catalogue raisonné. 4 vol. Paris et Bruxelles, 1928.

La Faille, J.B. de Vincent van Gogh. 1 vol. Paris: Hypérion, 1939.

Leymarie, J. van Gogh". Paris: Tisné, 1951.

Correspondance complète de Vincent van Gogh, trad. de M. Beerblock et L. Roelandt. Paris: Gallimard/Grasset, 1960.

Petit Larousse de la Peinture, sous la direction de Michel Laclotte. Paris: 1979.





## RESUME

Un long travail de recherche avait été entrepris pour déterminer si un tableau inconnu jusque là, attribué au peintre suisse Ferdinand Hodler, était une copie, voire un faux ou s'il avait été exécuté par l'artiste. Les examens scientifiques (rayons-x, u.v., réflectographie i.r., examens techniques et chimiques) n'avaient pas suffi pour établir avec certitude l'authenticité de l'oeuvre; alors que les documents historiques prouvaient que la peinture était sortie de l'atelier de Hodler. En dernier ressort la confrontation des deux tableaux en lumière transmise fournit la preuve déterminante recherchée.

Une méthode analogue permet une lecture plus aisée d'une composition sous-jacente à une oeuvre de Vincent van Gogh: la photographie en lumière transmise par un flash électronique vint compléter les résultats obtenus par d'autres examens.

L'USAGE DE LA LUMIERE TRANSMISE POUR L'EXAMEN DE DEUX PEINTURES MODERNES, L'UNE DE V. VAN GOGH (1887), L'AUTRE DE F. HODLER (1910)

Paolo Cadorin  
Picassoplatz, 8  
CH-4052 Bâle, Suisse

Monique Veillon  
Picassoplatz, 8  
CH-4052 Bâle, Suisse

Anne Trembley  
Kunstmuseum, Hodlerstrasse, 12  
CH-3011 Berne, Suisse

### Introduction

Une des missions de l'historien d'art est de donner des preuves pour affirmer ou contester l'authenticité d'une oeuvre; tâche particulièrement difficile car chaque époque a son vaste éventail d'activités "parallèles" à celle de l'artiste: de l'élève à l'imitateur, au copiste, au faussaire, qui peut facilement confondre même un observateur avisé. De nos jours, le chercheur peut être secondé par la collaboration de spécialistes de la conservation et de scientifiques de laboratoire. Les moyens d'examen mis à sa disposition sont chaque année plus nombreux et plus sophistiqués mais la confiance accordée au progrès des sciences peut nous induire parfois à négliger des méthodes simples mais aptes à résoudre un problème difficile.

### Historique du tableau de Hodler

Dans la production de Ferdinand Hodler (1853-1918), nombreuses sont les reprises d'un même sujet. L'apparition sur le marché en 1981 d'un tableau en tous points semblable à un original des années 1909/10 depuis longtemps reconnu comme authentique, ne fut pas une surprise: il s'agissait sans doute d'une réplique exécutée par l'artiste lui-même. (Fig. 1 et 2).

Celle-ci fut acquise dans une grande vente et portée après un certain temps par son nouveau propriétaire dans un institut de conservation pour un problème mineur concernant le support. Là, après plusieurs examens et analyses, les spécialistes déclarèrent qu'il s'agissait d'un faux.

Mais le tableau était doté d'un pedigree sans faille; de plus, le spécialiste de Hodler dont l'autorité faisait loi déclarait le tableau comme un original indiscutable.

Le tribunal, saisi par les deux parties, décida de remettre le dossier à un collège d'experts composé de deux historiens d'art



Figure 1 Hodler



Figure 2 Tableau incriminé

Figure 1

Ferdinand Hodler: Femme marchant.  
1909/10.  
Huile sur toile, 112 x 50 cm.

Figure 2

Tableau incriminé:  
Attribué à F. Hodler: Femme marchant.  
1910/11.  
Huile sur toile, 112 x 50 cm.

et d'un spécialiste de la conservation, et le chargea de trancher ce litige.

Les faits: étude du tableau "Femme marchant"

Les experts avaient à leur disposition les deux tableaux, et la possibilité de comparer ceux-ci dans des conditions d'étude optimales.

Pour l'oeuvre contestée, ils avaient aussi bien les arguments témoignant en faveur d'une attribution à Hodler que ceux prouvant la contrefaçon.

Pour l'attribution à Hodler ils avaient la certitude que le tableau provenait d'une collection prestigieuse constituée de nombreuses autres oeuvres de l'artiste avec lequel le collectionneur ainsi que sa soeur avaient entretenu des rapports d'amitié très étroits. De plus le tableau qui devait dater de 1911 environ, avait été exposé l'année suivante au "Sonderbund" à Cologne: les inscriptions et étiquettes sur le châssis, et une photographie retrouvée dans les archives de l'exposition en font foi. Enfin l'expert de Hodler, en possession de toutes les archives d'atelier du peintre et auteur d'importantes publications sur l'artiste, certifiait l'authenticité du tableau de manière péremptoire.

Contre l'attribution à Hodler, ils avaient les résultats de l'enquête technique faite par l'institut spécialisé: - le châssis était différent de ceux utilisés par Hodler habituellement; - la toile était d'une autre qualité; - la préparation était différente; - les pigments étaient d'une qualité inférieure; - la réflectographie i.r. laissait voir nettement sous la couche picturale un dessin préparatoire retenu, révélant l'effort fourni pour suivre des formes existantes et non libre et spontané comme l'était le dessin préparatoire de l'original. Ces lignes décalquées et d'autres encore, celles d'un quadrillage qui avait secondé le copiste, étaient présentées comme un argument déterminant contre l'attribution de l'oeuvre à Hodler.

Les experts chargés de l'enquête décisive, s'assurèrent tout d'abord que les résultats des analyses faites sur le bois, la toile et la couche picturale n'excluaient pas que l'oeuvre incriminée ait été exécutée à la même époque que l'oeuvre certifiée originale.

Une nette différence existait entre les éléments constitutifs des deux tableaux. Pour l'oeuvre certifiée authentique: châssis extensible à clefs, toile sombre patinée par la lumière, préparation blanche appliquée sur l'avant, pigments purs, de bonne qualité (dite "pour artistes"). Pour l'oeuvre mise en doute: châssis fixe en bois différent, toile claire, préparation grise appliquée sur l'arrière de la toile, pigments de qualité moindre (dite "d'études"). Mais si la science avait confirmé les différences perçues lors de l'observation à l'oeil nu, les résultats obtenus n'indiquaient en aucun cas que l'oeuvre contestée ait été exécutée postérieurement à l'original.

De plus, les étiquettes, timbres de douane et autres inscriptions apposées à l'arrière, sur le châssis de l'oeuvre contestée, étaient des originaux et témoignaient en faveur d'une datation possible dans les années 1910.

Par ailleurs, les conclusions tirées de la réflectographie i.r. révélant les lignes d'un quadrillage et d'un dessin préparatoire typique d'une copie, "donc d'une oeuvre non-originale", ces conclusions devaient être reconsidérées dans le cas présent; car chez Hodler la copie ou comme il la nommait lui-même, la "reproduction"<sup>4</sup>, faisait partie intégrante de son activité d'atelier. Hodler exécutait toujours une copie (pour mémoire) des tableaux dont il se séparait. Et pour que celle-ci se rapproche le plus possible de l'original, il employait la méthode du calque<sup>5</sup>.

Considérant les radiographies des deux tableaux, on doit reconnaître qu'elles donnent des images très différentes: celle de l'original, est très peu contrastée et révèle une distribution assez uniforme de la lumière (fig. 3); l'autre, vivement contrastée dénote une tout autre manière de travailler (fig. 4). Ces différences ne provenaient pas de variations dans l'exécution des documents radiographiques: les films utilisés, l'intensité des rayons, les temps d'exposition, les méthodes de développement étaient rigoureusement identiques<sup>6</sup>. La structure des deux tableaux n'était donc pas du tout la même et l'on pouvait se croire en possession d'un argument décisif; d'autant plus qu'un autre



Quatre radiographies exécutées dans des conditions identiques<sup>6</sup> et montrant que le tableau incriminé (fig. 4) offre une image très différente de celle du tableau Hodler (fig. 3); on trouve cependant des différences semblables dans d'autres oeuvres certifiées de Hodler, datant de la même époque (fig. 5 et 6).

#### Figure 3

F.Hodler: Femme marchant. 1909/10.  
Radiographie de la partie supérieure du tableau.

L'image peu contrastée est très différente de celle du tableau incriminé reproduite en fig. 4.



Figure 3: r-x HODLER 1909/10

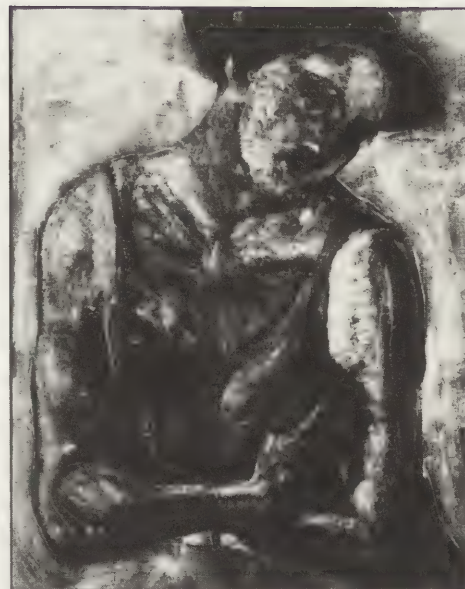


Figure 4: r-x tableau incriminé 1910/11

#### Figure 4

Radiographie du tableau incriminé: partie supérieure.

L'image très contrastée est tout à fait différente de celle donnée par la figure 3, mais peut être rapprochée de la radiographie reproduite en fig. 6.

#### Figure 5

F.Hodler: Autoportrait. 1912.<sup>7</sup>

Radiographie de l'ensemble du tableau.

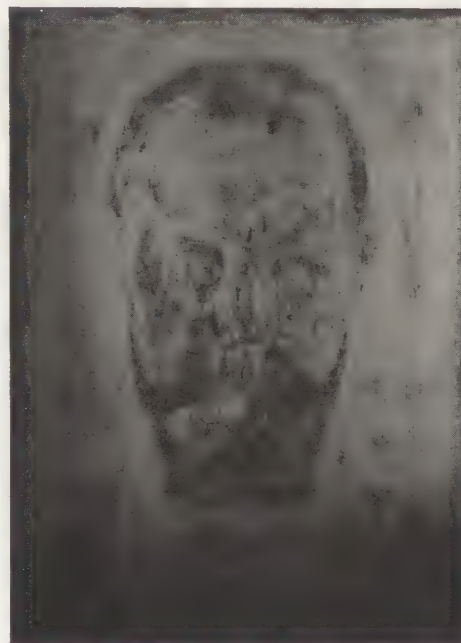


Figure 5: r-x HODLER 1912

#### Figure 6

F.Hodler: Figure de femme. 1910.<sup>8</sup>

Radiographie (partie supérieure)

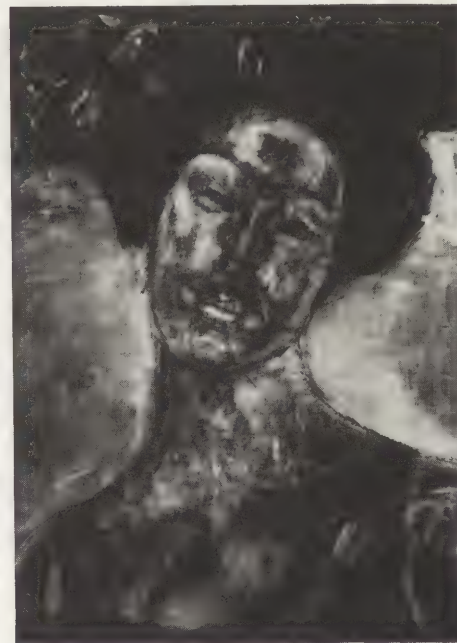


Figure 6: r-x HODLER 1910

original de Hodler en possession du Kunstmuseum de Bâle (fig. 5)<sup>7</sup> présentait une image radiographique étroitement apparentée à l'original certifié.

Il n'en était rien: la radiographie d'un troisième tableau de Hodler datant de la même époque (fig. 6)<sup>8</sup>, également propriété du Musée de Bâle, révélait cette fois-ci une structure étroitement apparentée à celle du tableau incriminé. Les observations résultant des examens aux rayons-x n'amenaient donc pas d'argument déterminant pour l'attribution du tableau.

Revenant, après toutes ces investigations, à l'examen à l'oeil nu, mettant à contribution la seule sensibilité de l'examineur, on pouvait résumer ainsi les différentes impressions sur le tableau incriminé:

- D'une manière générale, l'oeuvre n'avait pas la qualité de l'original certifié.
- Dans certaines parties comme le visage et surtout la partie des yeux, et des mains, la copie reprenait servilement - même si avec beaucoup d'habileté - les coups de pinceaux et la matière de l'original.
- Au deuxième plan, des nuances de couleur dues à des repentirs dans l'oeuvre originale avaient été elles aussi reprises "textuellement" (sans raison apparente) dans la composition.
- La signature était certainement apocryphe.



Quatre photographies en lumière transmise du tableau de Hodler (figures 7 et 8) et du tableau incriminé (figures 9 et 10).



Figure 7: HODLER / lumière transmise



Figure 9:  
tableau incriminé  
lumière transmise

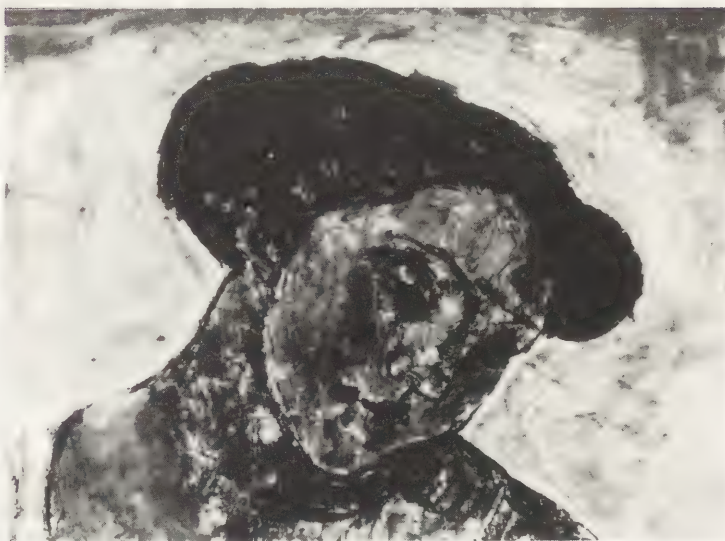


Figure 8: HODLER / lumière transmise



Figure 10: tableau incriminé  
lumière transmise

Tous ces éléments, en soi négatifs, laissaient entendre pour le moins une collaboration importante de l'atelier. Mais, d'autres observations permettaient de ne pas exclure la participation du maître: - Certaines parties (bras, jambes) de l'oeuvre incriminée étaient interprétées d'une manière très libre, différente de l'original.

- Des accents lumineux étaient donnés au moyen de couleurs tout à fait différentes, liberté que l'on ne saurait imputer à un élève copiant en d'autres endroits le maître d'une manière si fidèle.

Arrivés à ce point de la recherche, nous eûmes recours à l'observation par lumière transmise, cherchant des indications que les radiographies ne nous avaient pas données. Les deux tableaux furent placés côte à côte contre une grande baie vitrée et entourés d'un écran opaque pour permettre une meilleure vision (fig. 7 et 9). Dès cet instant, la différence d'écriture des deux tableaux sautait aux yeux: l'original révélait une recherche de la plasticité au moyen des masses d'ombre et de lumière brossées avec rapidité et décision (fig. 8); tout au contraire de la sage conduite du pinceau dans l'autre tableau dans lequel on reconnaissait l'application avec laquelle le peintre s'efforçait de suivre des lignes pré-établies (fig. 10). Même si Hodler avait copié lui-même son propre tableau, l'artiste n'aurait pu changer si radicalement sa technique picturale.



Grâce aux preuves tangibles apportées par cet examen le collègue d'experts fut en mesure d'exclure la participation de la main de Hodler dans l'exécution de l'oeuvre; mais à cause des documents irréfutables du pedigree, il dut considérer que le tableau avait sa place dans l'ensemble de l'oeuvre de l'artiste.<sup>10</sup>

L'examen en lumière transmise est tributaire principalement de la nature du support et de la technique d'exécution du tableau: tout élément opaque aux rayons lumineux dans la structure du support ou de la préparation exclura d'office l'usage d'un tel procédé.

#### Une méthode analogue appliquée à une oeuvre de Vincent van Gogh

Un tableau de V. van Gogh: "Les tournesols" 1887. <sup>11</sup> appartenant au musée des beaux-arts de Berne, devait être examiné, des lignes étrangères au sujet représenté laissant deviner une éventuelle composition sous-jacente (fig. 11).



Figure 11

V. van Gogh: Les Tournesols 1887.  
Huile sur toile, 50 x 60,7 cm.  
Berne, musée des beaux-arts.

Photographie en lumière normale.

Les examens habituels, tels que lumière tangentielle, loupe binoculaire, fluorescence u.v., réflectographie i.r., ne donnant que des informations insuffisantes, on eut recours aux rayons-x. Le musée ne possédant pas d'appareil radiographique, le tableau fut transporté à l'Institut suisse pour l'étude de l'art, à Zürich. L'image radiographique<sup>12</sup> révéla sous les tournesols la tête d'un homme portant un chapeau à large bord, incliné sur le côté, exécutée dans le sens vertical du tableau (fig. 12).



Figure 12

V. van Gogh: Les Tournesols 1887.

Radiographie dans le sens vertical du tableau.



C'est alors que le souvenir d'une conversation récente sur les possibilités offertes par la lumière transmise dans le cas d'un tableau de F.Hodler, ayant eu lieu au musée des beaux-arts de Bâle, donna l'idée d'une tentative dans ce sens. Mais dans ce cas la lumière naturelle ne suffisait pas à traverser l'épaisseur de la couche picturale.

Un examen au moyen d'une puissante source lumineuse artificielle<sup>13</sup> confirma la présence de la composition sous-jacente. La forte chaleur dégagée par la lampe ne permettait pas de prolonger suffisamment le temps nécessaire à un examen approfondi. Pour éliminer la chaleur, on pensa à une source lumineuse froide. Le flash électronique se révéla la source idéale pour obtenir une vision en lumière transmise des différentes couches.

Les bords du tableau se trouvant dans un état précaire de conservation, il fallait, pour les renforcer, détacher la toile du châssis. La nécessité de cette opération permit du même coup d'envisager une photographie en lumière transmise du tableau entier, sans l'ombre du châssis. La toile libérée du châssis et entourée d'un cache fut donc placée sur une plaque de verre posée sur deux tréteaux. Sous la plaque fut installé un flash électronique<sup>14</sup> couvert d'un verre dépoli pour une meilleure diffusion des rayons lumineux. L'appareil photographique<sup>15</sup> monté sur un statif cadrerait le tableau entier (fig. 13 et 14).

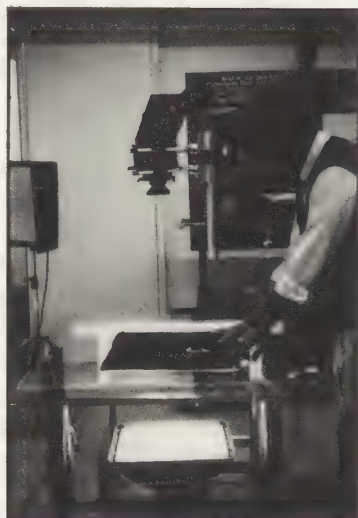


Figure 13 et 14

Photographie et croquis de l'installation ayant servi à exécuter le document reproduit en figure 15.

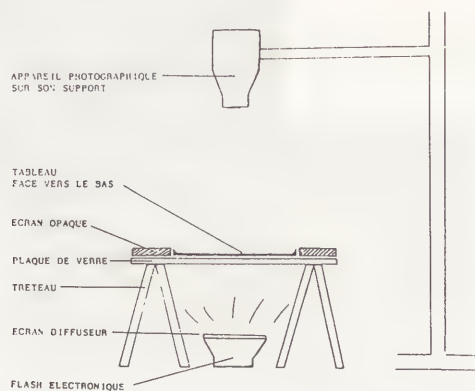


Figure 14

La photographie<sup>16</sup> fut prise dans l'obscurité, sous l'effet de 4 à 8 flash consécutifs. Le cliché obtenu par cette méthode nous donna des informations complémentaires, et plus précises que celles fournies par la radiographie: il ne s'agissait pas seulement d'une tête, mais du portrait en buste d'un homme attablé, tenant un verre à pied dans sa main gauche (fig. 15).



Figure 15

V. van Gogh: Les Tournesols 1887.

Photographie en lumière transmise avec flash électronique.



Cette dernière opération achevée, l'idée nous vint de refaire la réflectographie i.r., cette fois-ci par l'arrière du tableau. Le réflectogramme obtenu sur l'écran nous fournit encore d'autres informations sur la composition sous-jacente.

### Conclusion

Les méthodes scientifiques de recherche dans le domaine de la conservation nous offrent aujourd'hui une incroyable panoplie de possibilités pour l'approche de la vérité. Pourtant, quand pour différentes raisons il n'est pas possible d'y faire recours, ou quand les résultats attendus ne sont pas décisifs, ou ne sont pas atteints, des méthodes simples et peu coûteuses comme celles décrites ici peuvent donner des résultats intéressants.

### NOTES

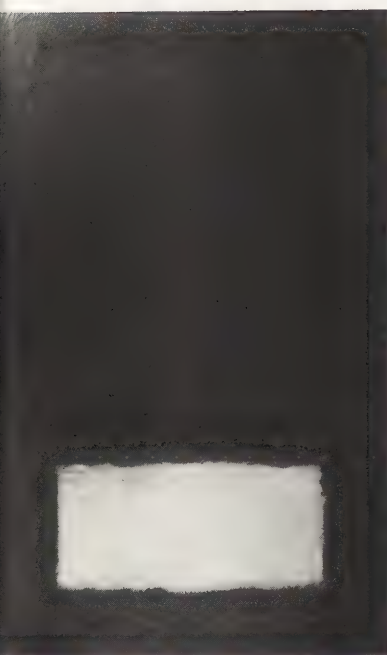
1. Le tableau original de Ferdinand Hodler: Femme marchant. 1909/10. Huile sur toile, cm 112 x 50. Coll. privée Suisse. Le tableau examiné: Attr. à Ferdinand Hodler: Femme marchant. 1910/11. Huile sur toile, 112 x 50 cm. Coll. privée, Suisse.
2. La participation du tableau incriminé à la sélection du Sonderbund à Cologne 1912, est attestée par une photographie qui se trouve dans le Rheinische Bildarchiv, sous le N° 32193.
3. Sur les couleurs et les liants utilisés par Hodler, voir: E. Linck, "Hodlers Maltechnik," in Technische Mitteilungen für Malerei, München 1. April 1934, p.51-52.
4. Hodler écrit dans une lettre du 1er septembre 1912: "Pour ce qui concerne la tête... je vous l'avais vendue avec la condition... que je voulais d'abord en faire une reproduction... elle m'appartient, aussi longtemps que je n'aurai pas fait cette copie". (Legs de l'artiste, lettre inédite).
5. R. Koella, "Zum zeichnerischen Werk," in Ferdinand Hodler (Catalogue d'exposition, Berlin-Paris-Zurich 1983) p.287. J. Brüscheiler, "Zu einigen Porträts und Selbstbildnissen: Entstehung, Deutung, Datierung," in ibid. p. 404. J. Brüscheiler, "Ursprung und Zweck von Hodlers zeichnerischem Werk," in Ferdinand Hodler Zeichnungen: vom Entwurf zum Bild, (Catalogue d'exposition, Winterthur-Solothurn-Innsbruck 1983) pp. 22-23. R. Koella, "Zur Kunstgeschichtlichen Bedeutung von Hodler's zeichnerischem Werk," in ibid. pp.50-53. "Gertrud Dübi-Müller photographies et documents" (Solothurn, Voigt-Schild AG 1984), p.51 et "Catalogue d'exposition Hodler" (Berlin-Paris-Zurich 1983) pp. 286-287 et pp.406-407: différents documents photographiques.
6. Appareil de radiographie Philips; 24 KV 15mA 30"; Film: Agfa X-ray Structurix D4.
7. Ferdinand Hodler: Autoportrait. 1912. Huile sur toile, 39 x 30 cm. Bâle, Kunstmuseum, Inv. G 1958.55.
8. Ferdinand Hodler: Figure de femme pour la composition "L'heure sainte". 1910. Huile sur toile, 180 x 90 cm. Bâle, Kunstmuseum, Inv. G 1958.53.
9. De plus, la matière picturale même, mise à nu par la transparence, différerait dans le tableau incriminé de toutes les peintures de Hodler de cette époque et présentait un réseau de craquelures prématurées atypique dans sa production.
10. Nous ne pouvons développer ici les nombreuses suppositions formulées sur la genèse de cette copie, les éléments certains étant trop peu nombreux pour les étayer.

11. Vincent van Gogh: Les Tournesols 1887. Huile sur toile, 50 x 60,7 cm. Signé en-bas à droite: Vincent 87. Berne, Kunstmuseum, Inv. 2140. La Faille N° 376, Hypérion N° 279. Douglas Cooper: Paul Gauguin: 45 lettres à Vincent, Théo et Jo van Gogh, (Lausanne, Bibliothèque des Arts, 1983) p.15. Ambroise Vollard, Souvenirs d'un marchand de tableaux, (Paris: A.Michel, 1937) p.66. Vincent van Gogh, Lettres à son frère Théo (Paris: Grasset, 1972) L. 571.
12. Appareil de radiographie Siemens: 20 KV 6 mA 6'; Film: Agfa X-ray Structurix D4P DW.
13. Lampe d'atelier type B, Elektro-Meilhaus, 8-Munchen 60. 8 tubes fluorescents: OSRAM-L-: - NATURA 20W/36 (2 x); - DAY-LIGHT 20W/15 (4 x); - WHITE-UNIVERSAL 20W/25 (2 x).
14. Flash Elinchrom, Theo Beeli AG Zurich, Studioflash. Illumination: 4000 W/sec.
15. Appareil photographique Sinar 4/5", objectif: Symar 150 mm, ouverture: 5,6 - 8.
16. Film Agfa-Pan 100 ASA. Exposition: 4 à 8 flash consécutifs.



## SUMMARY

The paintings of the "New York School" painter, Mark Rothko, are ageing at an accelerated rate. The combination of his experimental techniques and materials and the vulnerability of the paintings to environmental degradation have contributed to this deteriorating process. By briefly assessing the three mural projects that Rothko painted between 1958-1965, including their formulation and specific histories, factors which have precipitated the changes in the paintings can be established. Ultimately this information can be applied to Rothko's paintings in general, emphasizing preventative measures for their maintenance and treatment.



taking light photograph of a painting with stress cracks induced by the original trainer on which it is stretched

## EPHEMERAL PAINTINGS ON "PERMANENT VIEW"

## The Accelerated Ageing of Mark Rothko's Paintings

Dana Cranmer

Conservator of The Mark Rothko Foundation, Inc. New York City, USA

As a painter, Mark Rothko valued the immediate visual effect of his paintings over concern for their longevity. Along with many of his colleagues of the "New York School" of the 1950's, Rothko was an experimenter and an innovator. It was through his explorations in techniques and materials that he developed the extraordinary paintings that contain the special glowing quality that was distinctly his own. However, the consequences of his non-traditional approach are paintings that are extremely fragile and subject to accelerated ageing. They are overly responsive to changes in humidity and temperature and especially vulnerable to degradation through exposure to light.

As conservator of the Mark Rothko Foundation for the past six years, I have had the opportunity to become acquainted with the techniques and materials that Rothko developed over the forty years that he painted. Also, the conservation problems unique to Rothko's paintings became familiar territory.

The conservation concerns specific to Rothko's paintings require an interdisciplinary approach of conservation specialities: textile problems that result from the intimate relationship between the canvas support and the paint film; structural problems attributable to the inadequate wooden strainers Rothko used that were unstable and distorted, eventually transferring stresses to the paint film; and the problems inherent in the fragile paint film itself which is subject to cracking, abrasion and alterations from environmental effects.

Perhaps the most difficult and frustrating predicament for the conservator to address is the chemical alteration of the paint film. The phenomenon of fading has occurred in some of Rothko's paintings and is especially evident in the three mural projects that he painted: the "Seagram" murals (1958), the Harvard murals (1962), and the Rothko Chapel murals (1965). For each of the mural projects, Rothko produced a series of paintings from which he selected the works for final installation at the selected site. The Mark Rothko Foundation collection had a number of these "alternatives" for each of the mural projects with related studies both on canvas and on paper.

Many of the paintings in the three mural projects that Rothko chose for exhibition have changed appearance in some manner. These paintings are or have been on "permanent" view and have therefore been more subject to scrutiny. But, due to continuous exhibition, they are constantly exposed to the environment. Just how much this perpetual exposure, a requirement that Rothko himself established for these murals, has contributed to their rapid and premature deterioration is critical and merits investigation.

In sorting the factors that precipitated the changes in Rothko's mural paintings, attempting to ascertain the materials and techniques used in their creation is fundamental. Towards the end of the 1940s (prior to the mural projects which commenced in the late 1950s), Rothko transformed his painting style and technique. He discarded conventional preparation of the canvas and began to "stain" the canvas support with a solution of diluted rabbit-skin glue mixed with unbound quantities of powdered pigments, with subsequent layers of thinly-brushed oil and/or synthetic paint films. The paint film, its formulation and manipulation became the vehicle for Rothko's aesthetic explorations for the next thirty years of his life.

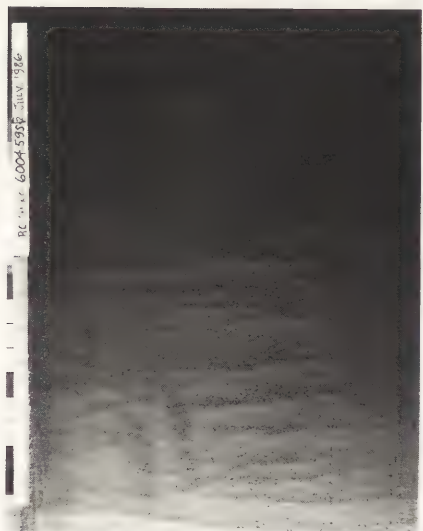
In his experiments with the paint formula, Rothko not only added whole eggs and powdered pigments, but in the painting process, he diluted the solution with unmeasured amounts of turpentine (in the case of oil paint) and water (in the case of synthetic paint). Often the painting medium was so extended by additions of solvent, that its physical coherence and integrity was compromised. The unbound pigment particles were left isolated, barely adhered to the canvas support. The resulting effect of radiant translucency was unique to Rothko's painting. The tenuous paint film permitted light to penetrate directly, its passage unencumbered by medium, to strike the individual pigment particles and bounce back, affording the viewer a rare experience of clear, resonant color.



However, the pigment particles are left unprotected from both mechanical and chemical forces. As there is very little bond between the particle and support, the surface is especially vulnerable to abrasion. Also, the pigment can be directly affected by the degrading elements of the environment.

In the mural projects, Rothko generally adhered to this preparation and painting procedure as described except for a few distinct variations. The "Seagram" mural project, commissioned in 1958 was Rothko's first attempt to create a series of related paintings that would be installed as an ensemble. They also were the largest paintings that he had ever attempted and he employed studio assistants to aid in the preparation and execution of the murals.

Though these murals were intended for installation in the Seagram building designed by Mies van der Rohe in New York City, they were withdrawn by the artist. Eventually nine of the series of some thirty paintings were given in 1969 to the Tate Gallery in London on the condition of their permanent installation. Over the years, some of the paintings have altered in appearance: a whitish "patination" developed on the surfaces. The specific causes have been difficult to identify because of the history of the paintings. In the ten years prior to their arrival in London, some of the paintings had been exhibited, some had received conservation treatment. (Rothko had a number of the paintings lined in preparation for their donation to the Tate Gallery.) The inherent fragility of the paintings, their history before London, and the subsequent some twenty years of exhibition at the Tate Gallery have all contributed to the alterations in the appearance of the paintings. There appears to be many, perhaps too many, contending factors that were influential to be able to extract a satisfactory analysis.



Detail of the surface of an "alternate" Seagram mural illustrating whitish streaks and overall cracks.

The second mural project, painted for Harvard University in 1962, presents a clearer case. These works have also significantly changed since leaving the artist's studio. For the Harvard series Rothko painted at least seven paintings, five of which (one triptych and two panels) were selected for installation in the penthouse faculty diningroom in the newly-built Holyoke Center. Rothko had complete control over the decoration of the room and installation of the paintings in the top floor room; a room which had large picture windows at either side.

Rothko painted the Harvard series using the same methods and materials as with the previous Seagram series, with a few additions. Rothko described to Elizabeth Jones, conservator of the Fogg Museum, that while working on the paintings, he had run out of paint and had purchased some paint at the local Woolworth's (a five and dime store). He told her that he had also applied an eggwhite solution in interleaving layers between paint films, a technique described by Cennini Cennino in his handbook and one used by Nicolas Poussin.<sup>1</sup>

Less than ten years after the paintings were installed, changes had appeared - especially in the center panel of the triptych. This particular painting had altered color dramatically and developed whitish streaks. In this case, unlike the Seagram murals which had complicating factors, the Harvard murals (except for a brief preview exhibition at the Guggenheim Museum in 1963) had been continuously installed in the Holyoke penthouse. In 1981, Harvard University (with the sanction of the Mark Rothko Foundation) removed the murals from the penthouse, and put them in storage. The Center for Conservation and Technical Studies at the Fogg Museum is preparing a technical study analyzing studies on paper that Rothko had made for the Harvard murals and it will include a history of the paintings. When this research is published, no doubt the complex interaction between the ingredients of Rothko's paintings and the environment will be better understood.

Rothko's last mural project, the Rothko Chapel in Houston, Texas, commissioned by Dominique and John de Menil in 1964, was his most ambitious project. Rothko executed over twenty very large paintings (ten by fifteen feet), fourteen of which would eventually hang in the Chapel that Rothko help design. The painting process and technique that Rothko developed for the Chapel works have been well-researched and documented by Carol Mancusi-Ungaro, conservator of the Menil Collection in Houston.<sup>2</sup> Through extensive interviews with Rothko's studio assistants and scientific analysis, she was able to determine that Rothko delegated the actual painting of the murals to his assistants, though always under his close scrutiny. The Chapel was composed using similar methods and materials developed for the other mural projects except for some



significant additions: charcoal under-drawings, synthetic paint films and dammar varnish crystals. Of the fourteen Chapel paintings that were finally installed, seven are "monochromes" - (variations of plum and wine color veils) and seven incorporate black rectangular forms floating on a plum color field. The black forms were first sketched in with charcoal over the plum background. After much editing, the desired shape was established and painted in with a layer of tube oil paint diluted with turpentine. The final layer, which Rothko formulated in unmeasured amounts, consisted of oil paint, turpentine, whole eggs and dammar resin.

The Chapel opened in 1971, a year after Rothko's death. In the subsequent decade the paintings containing the black form have developed whitish streaks which appear to correspond to the charcoal delineations beneath. The paint film has also developed extensive cleavage and accompanying losses which Carol attributes to the swelling of the undissolved dammar crystals responding to the humidity. Despite efforts to control the fluctuations of humidity and temperature, and construction of a skylight baffle, the murals have continued to deteriorate. Though the paintings have already altered in appearance, it is possible that conservation treatment could further compromise Rothko's original intention to an even greater extent.

In a sense, the mural projects serve as a large scale accelerated ageing test for gauging Rothko's paintings in general. In comparing the physical condition of the paintings in the Mark Rothko Foundation collection that were alternatives to the various mural projects, almost invariably they were in much better condition and thus closer to Rothko's intent than those that had been on "permanent" view. Most of the mural-related paintings in the Rothko Foundation collection had always been in storage and virtually never exhibited.

Certainly, the alterations in these mural paintings make it more than evident that Rothko's paintings in general, especially those created after the late 1940s, are delicate, acutely reactive to the environment, and require protection from its damaging effects.

As for the care and maintenance of the murals, all three institutions where the murals are installed have conservation departments that are involved in analyzing the paintings. Pigment identification and further analysis of the medium and techniques that Rothko used will aid enormously in caring for these works. Actual treatment for such chemical changes in the paint film may prove very problematic. Reversing the effects of ageing may require an alchemy that so far remains beyond our grasp.

#### Notes

1. Telephone conversation with Elizabeth Jones, March, 1987.
2. C. Mancusi-Ungaro, "Preliminary Studies for the Conservation of the Rothko Chapel Paintings: an Investigative Approach" (Paper delivered at the ninth annual meeting of the American Institute of Conservators, Philadelphia, May 27-31, 1981), p. 109.





# Working Group 7

Wet Organic Archaeological Materials

Matériaux organiques archéologiques  
gorgés d'eau





**MEMBERS**

J. Bill (Leichtenstein)  
 O. Braeker (Switzerland)  
 R. Clarke (England)  
 J. Coles (England)  
 C. Cook (Canada)  
 T. Daley (Canada)  
 M.L. Florian (Canada)  
 N. Gerassimova (U.S.S.R.)  
 G. Grosso (U.S.A.)  
 J. Hawley (Canada)  
 H. Jedrzejewska (Poland)  
 K. Jespersen (Denmark)  
 J. de Jong (Netherlands)  
 B. Lord (Canada)  
 I. MacLeod (Australia)  
 L. Murdock (Canada)  
 M.D. Parchas (France)  
 R. Saeterhaug (Norway)  
 K. Peters (New Zealand)  
 M. Sawada (Japan)  
 R. Schaudy (Austria)  
 F. Schweingruber (Switzerland)  
 R. Wallace (New Zealand)  
 J. Watson (England)  
 G. Young (Canada)

**TRIENNIAL OVERVIEW**

Coordinator  
 D.W. Grattan  
 (Canada)

Assistant Coordinator  
 P. Hoffmann  
 (Fed. Rep. Germany)

**PROGRAMME 1985-1987**

1. To conduct an international comparative project for the treatment of waterlogged wood.

Samples of wood from England, Japan, Canada, Australia, Norway and the Netherlands have been sent to 10 laboratories around the world to receive treatment, and also to 3 laboratories for analysis.

2. To encourage research into the sucrose treatment.

This method offers a cheaper alternative to PEG methods for instance, and initial results have been encouraging.

3. To study treatment methods for native New Zealand wood species.

These may have features which distinguish them from wood species elsewhere. Some have very high density, very high normal shrinkages and are very impermeable. This makes treatment very difficult.

4. To study the behaviour of unstable iron sulphides, which are frequently encountered in old samples of waterlogged wood.

5. To seek methods for treating waterlogged wood/metal composite artifacts.

**SUMMARY**

The Comparative treatment project is well advanced, and most of the samples are now treated and are ready for display at the next meeting of the Group in Fremantle.

Development of interest in sucrose treatments has continued. There have been studies in the U.S.A, Hungary and Canada. At least one laboratory (State Conservation Laboratory, Tallahassee Florida, U.S.A.) is constructing a large sucrose treatment facility.

A number of studies of wood/metal composites are underway, in Canada, England and Switzerland. In contrast to previous work there is more emphasis on the study of corrosion.

The Group underwent a name change. The new name more accurately describes the range of interests of this Working Group.

The group continues to circulate a Newsletter. The most recent was issue No. 16. Circulation has grown to approximately 750.

Thanks to R. Ramiere and M. Colardelle, Proceedings of the second ICOM Waterlogged Wood Working Group Conference have been published. (Grenoble, France, 1984)

A third special meeting has been held in Fremantle, Western Australia. This was a joint meeting with the Working Group on Metals, and focussed upon the problems of the wood/metal composite artifact.

**BIBLIOGRAPHY, 1984-1987****GENERAL**

Colardelle, M. "Le centre d'Études et de Traitement des Bois Gorges d'Eau, (Grenoble, France)," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 17-19.

- von Dienst, E. "Some Remarks on the Conservation of Wet Archaeological Leather," Studies in Conservation, vol. 30, (1985): pp. 86-92.
- Grattan, D.W. "Treatment of Waterlogged Wood," in Proceedings of the International Conference on Wet Site Archaeology, University of Florida, Gainesville (1986).
- Hart, C.A. "Relative Humidity, EMC and collapse shrinkage in Wood," Forest Products Journal, vol. 34, no.11/12, (1985) pp. 45-54.
- Hillman, D. and Florian, M.L. "A Simple Conservation Treatment for Wet Archaeological Wood", Studies in Conservation, vol. 30, (1985): pp. 39-41.
- Johannson, L.U. "Konservering av vattendrunkt organisk material (tra, lader, ban)," in Konserveringstekniska Studier, The Cultural Board of National Antiquities and Natural Historic Museums, Rapport T1, (Stockholm, 1983): pp. 98-103.
- Nemec, I. "Raziskava moknega lesa-studi j konservaijshih metodi (Research in Waterlogged Wood- a study in conservation methods," Part I, in Varstvo Spomenikov (1984):
- Paterakis, A. "Sintirisi Epbidrou Xilou (Conservation of Waterlogged Wood)," Archaiologia, no. 8, (1984): pp. 73-74.
- Rodriguez, D.A. "Consolidation of Archaeological Wood," Boletin Museo del Oro, no. 3, (1980): pp. 16-17.
- Smith, W.B., Cote, W.A., Sian, J.F., and Vasishth, R.C. "Interactions between Water-Borne Polymer systems and the Wood Cell Wall," Journal of Coatings Technology, no. 57, no. 729, (1985): pp. 27-35.

#### COMPOSITES

- Cook, C., Dietrich, A., and Grattan, D.W. "Experiments with treatments for waterlogged wood-metal objects," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 147-159.
- Cook, C. "Tests of Resins for the Treatment of Composite Objects," ICOM Working Group on Wet Organic Archaeological Materials Newsletter, no. 14, (1986): pp. 3-5.
- O'Donnell, E.B., and Julian, M.M. "Conservation of a Dissassembled British Naval Hand Grenade," in Proceedings of the Sixteenth Conference on Underwater Archaeology, ed. P.F. Johnston, Special publication series, Society for Historical Archaeology, no. 4, (1985): pp. 80-81.

#### DETERIORATION AND ANALYSIS

- Barbour, R.J. "The condition and dimensional stabilization of highly deteriorated waterlogged hardwoods," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 23-38.
- Clarke, R.W., and Squirrell, J.P. "The Pilodyn- An Instrument for Assessing the Condition of Waterlogged Wooden Objects," Studies in Conservation, vol. 30, no. 4, (1985): pp. 184-188.
- Eenkhoorn, W., and Wevers, A.J.M.; Report of an investigation into wood and soil samples in the area of the East Indiaman Amsterdam, Rijksdienst voor de IJsselmeerpolders Report, no. 28 abw (1983).
- Grattan, D.W., and Mathias, C. "Analysis of waterlogged wood: The value of chemical analysis and other simple methods in evaluating condition," Somerset Levels Papers, vol. 12, (1986): pp. 1-12.



Hoffmann, P., Peek, R.D., Puls, J., and Schwass, E. "Das Holz der Archäologen, Untersuchungen an 1600 Jahre altem wassergesättigten Eichenholz der "Mainzer Romschiffe," Holz als Roh-und-Werkstoff, vol. 44, (1986): pp. 241-247.

Jespersen, K. "Extended storage of waterlogged wood in nature," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramière and M. Colardelle, (Grenoble, September 28, 1984), pp. 39-54.

Matsuda, T. "On reducing the shape of the tissues of the dried and shrunk waterlogged wood for the identification of its species," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramière and M. Colardelle, (Grenoble, September 28, 1984), pp. 55-62.

Shigo, A. "Compartmentalization of Decay in Trees," Scientific American, April (1985): pp. 96-103.

Sturla, A. "L'informatique comme aide à la décision dans le traitement des bois gorgés d'eau," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramière and M. Colardelle, (Grenoble, September 28, 1984), pp. 161-165.

#### PEG IMPREGNATION etc.

Barka, G., Knauer, H., and Hoffmann, P. "Simultaneous Separation of Oligomeric and Polymeric Ethylene Glycols (DP 1-110) Using Reverse Phase HPLC (HRPLC)," To appear in J. Chromatography (1986/7).

Hoffmann, P. "On the stabilization of waterlogged oakwood with PEG-Molecular size versus degree of degradation," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramière and M. Colardelle, (Grenoble, September 28, 1984), pp. 95-116.

Hoffmann, P. "On the stabilization of waterlogged oakwood with PEG II," Studies in Conservation, vol. 31, no. 3, (1986): pp. 103-113.

Hoffmann, P. "Zur Restaurierung Mittelalterlicher Daubengefasse mit Polyethyleneglycol," Arbeitsblätter für Restauratoren, vol. 2, group 8, (1984): pp. 98-111.

Hon, D.N.S., Chang, S.T., and Feist, W.C. "Protection of Wood Surfaces Against Photooxidation," Journal of Applied Polymer Science, vol. 30, (1985): pp. 1429-1448.

Laures, F.F. "A Means of Rapid Drying of Antique Wooden Material Previously Saturated With Polyethylene Glycol," International Journal of Nautical Archaeology, vol. 13, no. 4, (1984): pp. 325-327.

Laures, F.F. "More details about rapid drying of wood by frying in polyethylene glycol," International Journal of Nautical Archaeology, vol. 15, no. 1, (1986): p. 66.

Mills-Reid, N.K. "Polyethylene Glycol versus Glycerol, the Importance of Molecular Structure," ICCM Bulletin, vol. 12, (1986).

Sawada, M. "Some problems of setting PEG 4000 impregnated in wood (contraction of impregnated PEG solutions upon setting and its effects on wood," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramière and M. Colardelle, (Grenoble, September 28, 1984), pp. 117-124.

#### IMPREGNATION BY SUCROSE AND RELATED MATERIALS

Murray, H. "The use of Mannitol in Freeze-Drying Waterlogged Organic Material," The Conservator, no. 9, (1985): pp. 33-35.

Parrent, J.M. "The Conservation of Waterlogged Wood Using Sucrose," Studies in Conservation, vol. 30, (1985): pp. 63-72.

Parrent, J.M. "The Conservation of Waterlogged Wood Using Sucrose," in Proceedings of the Sixteenth Conference on Underwater Archaeology, ed. P.F. Johnston, Special publication series, Society for Historical Archaeology, no. 4, (1985): pp. 83-95.

### IMPREGNATION BY MATERIALS OTHER THAN PEG

- Ginier-Gillet, A., Parchas, M.D., Ramiere, R., and Tran, Q.K. "Méthodes de conservation développées au C.T.B.G.E. (Grenoble-France): impregnation par une résine radiodurcissable et lyophilisation," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 125-139.
- Haas, A. "Nassholzkonservierung (Arigal-C/Lyofix DML)", ICOM Working Group on Waterlogged Wood Newsletter, no. 12, (1984).
- Haas, A. "Neue Entwicklung bei der Nassholz-Konservierung mit Melamin Formaldehyd Kondensation," Arbeitsblätter für Restauratoren, vol. 18, no. 8, (1985).
- Kazanskaya, S.Y., and Nikitina, K.F. "On the conservation of waterlogged degraded wood by a method worked out in Minsk", in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 139-146.
- Schaudy, R., Wendrinsky, J., Kalteis, H., Grienauer, W., and Slais, E. "Strahlungshartbare Imprägniermittel für die Konservierung archaologischer Holzfunde (Teil 3) und weitere Konservierungsversuche an intakten und künstliche abgebauten Holzproben," Osterreichisches Forschungszentrum Seibersdorf, OEFZS 4346, CH 357/86 (1986).

### FREEZE-DRYING

- Amoignon, J., and Larrat, P. "Traitement des bois gorgés d'eau par lyophilisation. Application aux objets des grandes dimensions," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 181-186.
- Cook, C. and Grattan, D.W. "A practical comparative study of treatments for waterlogged wood -Part III- Pretreatment solutions for freeze-drying," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 219-240.
- Drocourt, D., and Morelle-Deledelle, M. "Reflexions après deux années de conservation de l'épave de la Bourse à l'état lyophilisé," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 187-188.
- Drocourt, D., and Morelle-Deledelle, M. "Marseille, lyophilisation la pression atmosphérique d'une épave de bateau romain," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 169-174.
- Fry, M.F. "An economy vacuum freeze/dryer for archaeological organic materials," Vacuum, no. 5, (1984): pp. 555-558.
- Hug, B. "Lyophilisation: 10 ans d'expérience," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 207-212.
- Janniere, G. and Meurges, G. "Traitement des bois gorgés d'eau par la technique de lyophilisation au Museum National d'Histoire Naturelle," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 175-180.
- Saeterhaug, R. "Investigations concerning the freeze-drying of waterlogged-wood conducted at the University of Trondheim," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 195-206.
- Schaudy, R., and Slais, E. "Zur Konservierung von Nassholz durch Gefriertrocknung und Harztrankung. Teil 1: Einfluss der Vorbehandlung auf das Trocknungsergebnis," in Osterreichisches Forschungszentrum Seibersdorf, OEFZS 4350, CH 360/86 (1986).



Schaudy, R., and Slais, E. Konservierung neolithischer Nassholzfunde nach der Methode PEG-Gefriertrocknung," in Österreichisches Forschungszentrum Seibersdorf, OEFZS 4335, CH 351/85 (1985).

Schaudy, R., Marius, M., and Slais, E. "Konservierung neolithischer Schnunr- und Geflechtreste durch Gefriertrocknung," in Österreichisches Forschungszentrum Seibersdorf, OEFZS 4361, CH 351/86 (1986).

Schaudy, R., Eibner, C. and Slais, E. "Konservierung eines mittelalterlichen Steigbaumes durch Gefriertrocknung und Harztrankung," in Österreichisches Forschungszentrum Seibersdorf, OEFZS 4341, CH 355/85 (1985).

Watson, J. "Research into aspects of freeze-drying hardwoods, between 1982 and 1984," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 213-217.

#### TREATMENT OF SHIPWRECKS ETC.

Anon, Annual Report, Mokpo Conservation and Research centre (1985). Cultural Property Research Institute, Korea. (PEG treatment of the Shinan Wreck)

Bouis, J. "Le sauvetage de l'épave de l'Anse Gerbal à Port-Vendres (Pyrenees-Orientales)," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 89-92.

Grattan, D.W. "Some Observations on the Conservation of Wooden Shipwrecks," ICCM Bulletin, vol. 12, (1986).

Hafors, B. "The drying pattern of the outer planking of the Wasa hull," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 313-326.

Hamilton, D.L. "Preliminary Report on the archaeological investigations of the submerged remains of Port-Royal, Jamaica, 1981-1982," The International Journal of Nautical Archaeology, vol. 13, no. 1, (1984): pp. 11-15.

Hoffmann, P. "The Bremen Cog Sails a New Course," The International Journal of Nautical Archaeology, vol. 15, no. 3, (1986): pp. 215-220.

Lord, B. "Projet pour la conservation de l'Hamilton et du Scourge", deux navires armés pour la guerre de 1812," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 261-268.

Pomey, P. "Les eaux maritimes: la Direction des Recherches Archéologiques Sous-Marines," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 9-13.

Seifert, B., and Jagels, R. "Conservation of Ronson ship's bow," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 269-298.

#### TERRESTRIAL WET SITES.

Bocquet, A. "Les eaux intérieures: le Centre National de Recherches Archéologiques Subaquatiques," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 13-16.

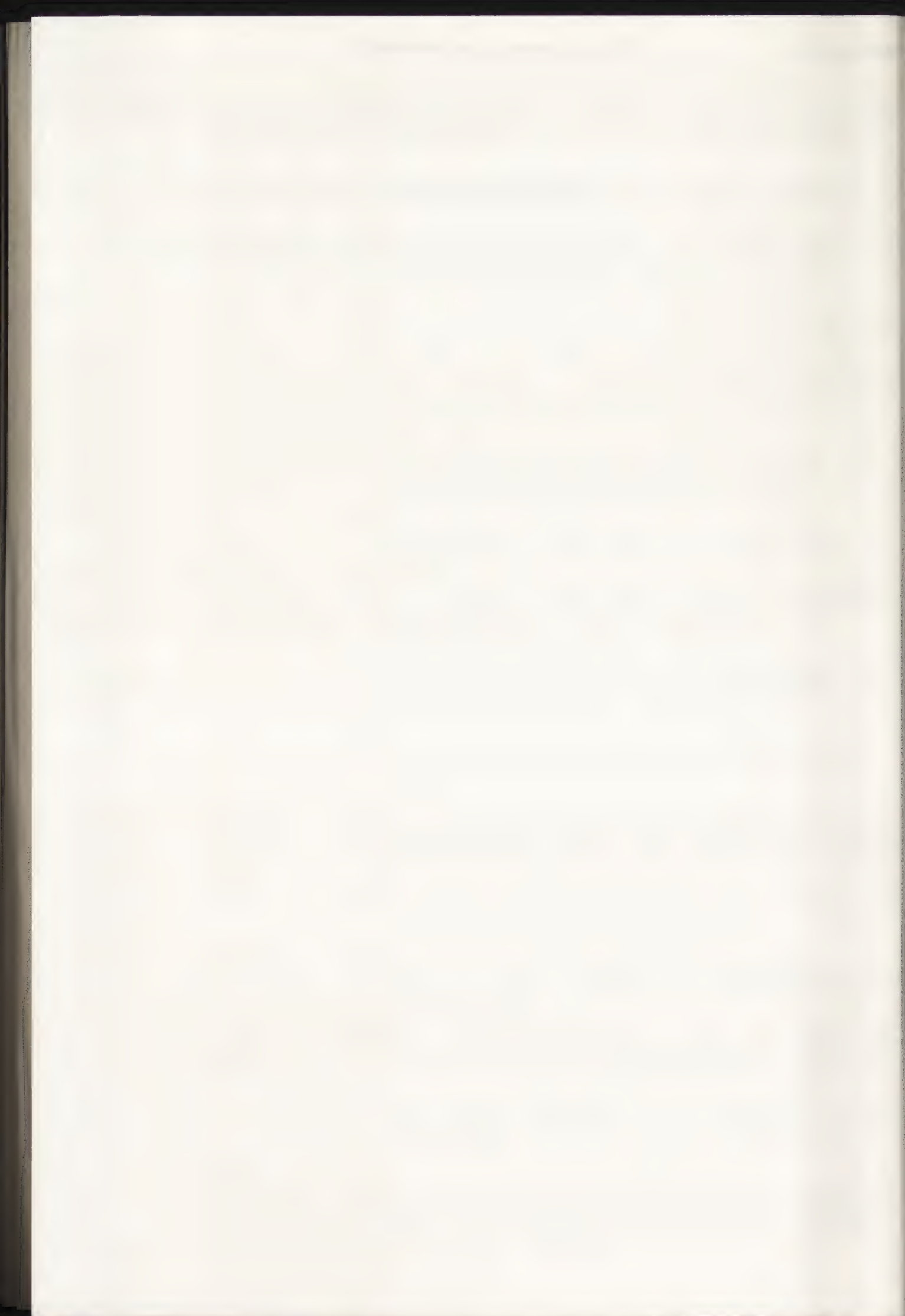
Coles, B. "Archaeological Techniques in a Wetland Context: The Somerset Levels", in Proceedings of the International Conference on Wet Site Archaeology, University of Florida, Gainesville (1986).

Coles, J. "Irish Wetlands: The Last Chance," in Proceedings of the International Conference on Wet Site Archaeology, University of Florida, Gainesville (1986).

- Coles, J. "Bog Bodies of Northern Europe," in Proceedings of the International Conference on Wet Site Archaeology, University of Florida, Gainesville (1986).
- Coles, J. "Precision and Purpose in Wet Site Archaeology," in Proceedings of the International Conference on Wet Site Archaeology, University of Florida, Gainesville (1986).
- Colardelle, M. "Le gisement medieval de Colletière à Charavines (Isere-France): de la fouille au traitement," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 71-80.
- Daugherty, R. "Responsibilities and Commitment in the Excavation of Wet Sites," in Proceedings of the International Conference on Wet Site Archaeology, University of Florida, Gainesville (1986).
- Denton, M.H.; and Gardner, J.S. "The Recovery and Conservation of Waterlogged Goods from the Well excavated at the Fort Loudon Site," Historical Archaeology, vol. 17, no. 1, (1983): pp. 96-103.
- De Witte, E., Terfve, A., and Wynckier, J. "La consolidation du bois gorges d'eau des bateaux gallo-romains de Pommeroeul," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 339-348.
- De Witte, E., Terfve, A., and Vynckier, J. "The Consolidation of the Waterlogged Wood from the Gallo-Roman boats of Pommeroeul," Studies in Conservation, 29, (1984): pp. 77-83.
- Doran, G.H., and Dickel, D. "Multidisciplinary Investigations at the Windover Site," in Proceedings of the International Conference on Wet Site Archaeology, University of Florida, Gainesville (1986).
- Egloff, M. "Recent Archaeological Discoveries in Lake Neuchatel (Switzerland): from the Paleolithic to the Middle Ages," in Proceedings of the International Conference on Wet Site Archaeology, University of Florida, Gainesville (1986).
- Gilland, M.S. "Marco's Buried Treasure: Wetlands Archaeology and Adventure in Nineteenth Century Florida," in Proceedings of the International Conference on Wet Site Archaeology, University of Florida, Gainesville (1986).
- Johnson, R. "Large waterlogged timber structures excavated on the Billingsgate excavation," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 63-70.
- van der Leeuw, S.E. "Some Aspects of Wet Site Archaeology in the Netherlands," in Proceedings of the International Conference on Wet Site Archaeology, University of Florida, Gainesville (1986).
- Nielsen, H.O. "The treatment of waterlogged wood from the excavation of the Hathaibu Viking ship," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 299-312.
- Nielsen, H.O. "Die Konservierung des Wikingerschiffes und des Nassholzfunde aus dem Hafen von Haithabu," Arbeitsblätter für Restauratoren, vol. 18, no. 8, (1985).
- Purdy, B.A. "The Significance of Archaeological Wet Sites: Hontoon Island, a Florida Example," in Proceedings of the International Conference on Wet Site Archaeology, University of Florida, Gainesville (1986).
- Schweizer, F., Houriet, C., and Mas, M. "Controlled air drying of large Roman timber from Geneva," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 327-338.



- Spriggs, J.A. "Treating the Coppergate Structures- A Quest for Anti-Shrink Efficiency", in Archaeological Papers from York Presented to M.W. Barley, ed. P.V. Addyman and V.E. Black (York: 1984), pp. 78-863.
- Tuck, J.A. "A Technique for the Excavation of Small Ponds," in Proceedings of the International Conference on Wet Site Archaeology, University of Florida, Gainesville (1986).
- Wallace, P. "The survival of wood in tenth to thirteenth century Dublin," in Proceedings of the Second ICOM Waterlogged Wood Working Group Conference, ed. R. Ramiere and M. Colardelle, (Grenoble, September 28, 1984), pp. 81-88.





## RÉSUMÉ

Cette communication présente une partie des données recueillies lors du traitement de six embarcations découvertes durant la construction du Musée de la civilisation à Québec. Une tentative de traitement par séchage à froid avec pré-traitement au P.E.G. 400 fut effectuée à l'hiver 1986 avec des résultats peu concluants. Les résultats préliminaires d'une autre tentative effectuée à l'hiver 1987 semblent beaucoup plus prometteurs et démontrent une forte corrélation entre le pourcentage quotidien de perte en poids et les conditions climatiques ambiantes, particulièrement le degré d'ensoleillement et la vitesse du vent.

## SUMMARY

This paper is based on some of the data gathered during treatment of six boats which were discovered during the construction of the Musée de la civilisation in the city of Québec. A trial freeze-drying project, following pretreatment with PEG 400, was conducted during the winter of 1986 with inconclusive results. Preliminary results of a subsequent experiment (winter 1987) appear to be much more promising and demonstrate a striking correlation between the daily percentage loss in weight and the ambient conditions, particularly in reference to the amount of sunshine and the wind velocity.

## LE SÉCHAGE À FROID EN MILIEU EXTÉRIEUR: EVALUATION DE L'EFFICACITÉ DE L'HIVER QUÉBÉCOIS

André Bergeron  
Restaurateur, archéologie et ethnologie  
Centre de conservation du Québec  
Ministère des Affaires culturelles  
476, rue Desrochers  
Ville Vanier, Québec, Canada  
G1M 1C2

Introduction: Historique du projet

Dans le cadre des travaux de construction du Musée de la civilisation à Québec, les vestiges de six embarcations furent mis au jour de octobre 1984 à mars 1985.

Une première embarcation découverte en 1974 avait été réenterrée à l'époque à cause de l'inexistence de l'expertise et de l'infrastructure pour effectuer le traitement. Dix ans plus tard, lors du début des travaux en octobre 1984, il devenait urgent de préserver ce vestige que l'on croyait unique. Cette opération de sauvetage constitua une occasion spéciale de collaboration entre l'archéologie et la conservation en permettant le développement d'une stratégie d'intervention qui tienne compte des nécessités de la fouille au niveau de l'enregistrement des données et de la conservation du bois gorgé d'eau. La découverte ultérieure en janvier et en mars 1985 de plusieurs autres embarcations de taille et de fonctions différentes vint complexifier le traitement en raison du manque de ressources humaines et matérielles.

Deux modes d'intervention furent utilisés sur le chantier de fouille: dans le cas des embarcations légères (bateaux à fond plat), il fut décidé de les démembrer et de les transporter pièce par pièce dans un bassin rempli d'eau en attendant le pré-traitement (nettoyage, documentation et P.E.G. 400). Les deux autres embarcations à voile, plus longues, plus lourdes et d'un assemblage plus complexe furent soulevées telles quelles, au moyen d'un dispositif d'arrimage sur mesure. Le but de cette opération était d'éviter d'interrompre les travaux de construction du Musée, d'effectuer l'enregistrement des données à un autre endroit et d'éviter de briser les pièces de bois encore gelées à ce moment.

Compte tenu de l'ampleur du projet, nous avons opté pour deux solutions de séchage dictées par la dimension des objets à traiter. Les deux embarcations à voile furent transportées sur un emplacement temporaire où elles étaient maintenues humides au moyen d'un système de boyaux d'arrosage pour le jardinage. Un local fut trouvé et une enceinte à micro-climat fut construite sur mesure afin de permettre le traitement du bois au moyen de polyéthylène glycol 400 et 540 avec abaissement progressif de l'humidité relative.

Les embarcations à fond plat furent préparées et installées dans des bassins construits sur mesure avec du contre-plaqué et du polyéthylène en rouleau. La concentration en P.E.G. fut augmentée progressivement sur une période d'une année pour atteindre une valeur moyenne de 39%. Parallèlement à tous ces préparatifs, la préparation des plans de forme et de reconstitution des embarcations fut effectuée par l'équipe d'archéologues. De nombreuses analyses furent également effectuées pour les pièces de lest, pour déterminer la composition des résines et du calfeutrage, la datation par dendrochronologie, l'identification des essences de bois et la cueillette de données sur la technologie maritime (1). Le potentiel de l'hiver canadien pour effectuer le traitement du bois gorgé par séchage à froid avait déjà été exploré par Grattan, Mc Cawley et Cook en 1978 et 1980 avec de bons résultats. Le choix de cette méthode s'est imposée comme le seul choix logique pouvant être retenu afin de traiter économiquement ces quantités importantes de bois.

Le séchage à froid de l'hiver 1986: Contexte et évaluation du résultat.

La première expérience fut effectuée du 6 janvier 1986 au 26 mars 1986 dans une serre désaffectée réaménagée pour la circonstance.



PHOTO 1



Le prélèvement de la pirogue retrouvée dans un lac du nord de Montréal, à l'été 1986. Code Borden: CaFk-1  
Photographie: Anne-Marie Balac, M.A.C.

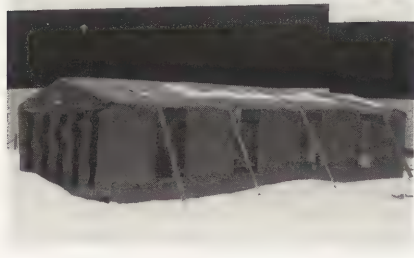
Les vestiges de trois des embarcations à fond plat furent séchées à froid et lorsque la température ambiante arriva aux alentours de 0°C, les pièces de bois furent installées à l'intérieur d'une enceinte à micro-climat afin de permettre au bois de se rééquilibrer à une valeur plus basse d'humidité relative. La température du bois en surface et à environ 1cm. en profondeur était enregistrée, de même que la température ambiante. La pièce d'étrave (No. 12A9-1) fut choisie comme témoin de l'évolution du traitement au niveau de l'apparence générale et du changement de poids. Après 4 jours, la pièce avait développé un réseau de craquelures en surface, contrairement aux autres pièces beaucoup plus petites et d'une faible épaisseur (3 à 5 cm) dont l'apparence n'avait pas changée. D'un poids de 11,060 gr. au départ, la pièce à la fin du traitement avait perdu seulement 970 g., ce qui représente une perte en poids de seulement 8,8%, ce qui est très loin du 50% anticipé (2). L'humidité relative dans la serre se situait aux alentours de 95-98%. A la fin de mars, le bois fut rentré à l'intérieur et après 11 mois de séjour dans l'enceinte à micro-climat, la pièce fut pesée à nouveau. Le 17 février 1987, elle avait perdu un autre 4,200 gr. ce qui signifie une perte totale de 5,170 gr, pour un pourcentage de 46,7%. La perte principale en poids s'est donc produite lors du séchage contrôlé et non pas lors du séchage à froid tel que prévu.

Après une brève période de remise en question du procédé et d'analyse des résultats, nous avons remarqué un certain nombre de problèmes reliés au design et à l'emplacement de l'abri extérieur. Le manque de ventilation créait une humidité beaucoup trop élevée à l'intérieur, ce qui nuisait au processus. Ce facteur combiné au manque de soleil dû à la présence de neige sur le toit, explique ce pourcentage si faible de perte d'eau. Malgré ce résultat décevant, la bonne apparence des pièces après traitement nous a incité à aller de l'avant et à poursuivre nos essais lors de l'hiver 1987.

#### Le séchage à froid de l'hiver 1987: Résultats préliminaires

Nous avons abandonné en 1987 le design de la serre pour une structure de garage en toile avec de légères modifications. Le garage est orienté d'ouest en est de façon à profiter au maximum des vents dominants; les deux extrémités peuvent s'ouvrir afin d'accélérer le renouvellement de l'air sec et de maximiser le déficit en humidité. La partie exposée au sud présente également des ouvertures transparentes afin de permettre à la lumière solaire de pénétrer et d'apporter un peu d'énergie au système.

PHOTO 2



Vue latérale de l'abri utilisé à l'hiver 1987 pour le séchage à froid. A remarquer: le design des portes qui permet à l'air de circuler tout en bloquant la neige ainsi que les ouvertures au sud afin de permettre la pénétration de la lumière solaire.  
Photographie: A. Bergeron, M.A.C.

PHOTO 3



Vue de l'intérieur de la tente montrant les tablettes latérales sur lesquelles les pièces de bois sont déposées, ainsi que la pirogue avec les sondes de température.

Photographie: Guy Couture



PHOTO 4



ue de la partie avant de  
a pirogue. A remarquer le  
ystème de soutien pour le  
ôté gauche, fissuré à par-  
ir de la base, ainsi que  
es traces de l'outillage  
utilisé lors du façonnage.  
Photographie: Claude Payer,  
M.A.C.

Deux objets ont été placés à l'intérieur; la dernière embarcation à fond plat (No. 8C1) du Musée de la civilisation et une pirogue monoxyle en pin blanc découverte à l'été 1986 dans un lac du nord de Montréal (3). Le pré-traitement a légèrement varié dans les deux cas: 8C1 a été imprégné avec du P.E.G. 400 dont la concentration a été augmentée graduellement de 10% à 35% sur une période de plus d'une année, tandis que la pirogue a reçu une imprégnation de deux mois au P.E.G. 400 à 10% avec un 5% supplémentaire de P.E.G. 540 liquide rajouté dans le bassin pour une période de 3 mois. De plus, lors de l'installation à l'extérieur, du P.E.G. 540 fut brossé sur toute la surface de la pirogue afin de compléter le pré-traitement.

Les résultats sont jusqu'à présent très encourageants. Après un mois et demi de séchage, la perte en poids par rapport au poids initial est d'environ 20% pour l'embarcation 8C1 et de 34% pour la pirogue. Lors du prélèvement d'échantillons pour la datation par dendrochronologie, la sonde a heurté la glace à environ 6cm de la surface ce qui donne une idée de la pénétration du P.E.G. à l'intérieur du bois. De plus, une amélioration très nette a été remarquée entre le pourcentage de perte de poids quotidien, la vitesse du vent et l'ensoleillement entre deux pesées.

Le seul problème concerne l'entrée éventuelle de neige à l'intérieur dans le cas d'une tempête imprévue. Le bois se comporte très bien depuis le début du séchage et lorsque la température se réchauffera, le bois sera placé à l'intérieur d'une enceinte à micro-climat afin de le rééquilibrer progressivement à une valeur plus basse de l'humidité relative.

PHOTO 5



Vue de quelques pièces en cours de séchage sur une des tablettes de la tente.

Photographie: Claude Payer, M.A.C.

#### NOTES

- (1) De nombreux organismes et personnes ont participé de près ou de loin à la recherche sur les embarcations. Je tiens ici à remercier M. Louis Laflèche de Parcs Canada pour l'identification des essences de bois, M. Pierre St-Julien du département de géologie de l'Université Laval pour l'identification des pierres de test, l'équipe du laboratoire de police scientifique de Montréal pour leur travail sur la détermination des résines et le calfeutrage, Madame Louise Filion et son équipe du Centre d'études nordiques de l'Université Laval pour la dendrochronologie, à MM. Gilbert Filion et Louis-Philippe Allard, du service de l'environnement atmosphérique, Environnement Canada, pour les données météorologiques, M. Daniel Laroche, archéologue et son équipe pour la collaboration constante démontrée lors de la fouille, à MM. Adéodat Tremblay et Jacques Boudreault pour leur magnifique travail de mise en forme de l'embarcation à voile 10C3, Madame Lise Jodoin pour son aide lors de la récupération des vestiges, et ceux qui ont travaillé dur pour la conservation des embarcations: Madame Lyne Gravel, M. Michel Plamondon et M. Gilles Chartier. Je tiens à remercier d'une façon spéciale mon bras droit Madame Francine Rémillard et MM. Michel Cauchon et Claude Payer pour l'enthousiasme et la motivation.

- (2) Le contenu en eau pour les pièces du Musée est assez élevé: 10C3-10= 687%, 10C3-11= 543%, 10C1-12= 585% et 10C3-13=703%, tandis qu'il est plus bas pour la pirogue avec une mesure de 282%.

La détermination du contenu en eau s'est effectuée de la façon suivante:

$$\frac{\text{Poids mouillé} - \text{poids sec} \times 100}{\text{Poids sec}}$$

- (3) Nos remerciements à Ville Vanier pour nous avoir donné la permission d'installer notre garage sur le terrain de leur station de pompage à l'hiver 1987.

FIGURE 1

Évolution de la perte en poids pour la pirogue exprimée en % du poids initial en relation avec la vitesse moyenne du vent à chaque mesure.

Pourcentage de perte

Vitesse du vent (Km/h.)

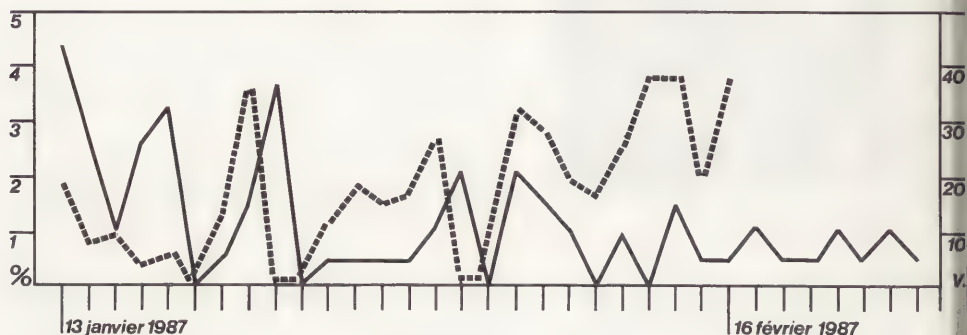
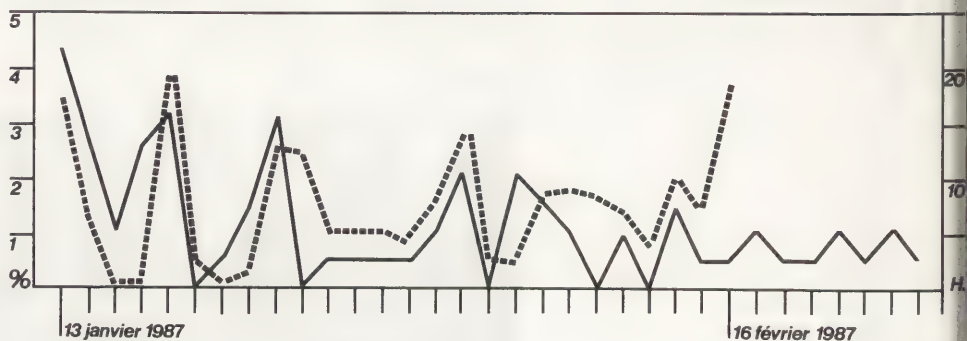


FIGURE 2

Évolution de la perte en poids pour la pirogue exprimée en % du poids initial en relation avec le nombre d'heures d'ensoleillement à chaque mesure.

Pourcentage de perte

Degré d'ensoleillement



## BIBLIOGRAPHIE

- Bergeron, André, "Conservation et archéologie au Québec", dans les résumés de la 2e conférence de l'ICROM sur les mesures de protection sur le site, tenue à Gand, novembre 85.
- Bergeron, André, Cauchon, Michel, "Le mystère du garage de toile" dans *Inter Mac*, Vol. 6, n. 8, Janvier-Février 1987.
- Bergeron, André, La Roche, Daniel, "Sous le Musée de la civilisation", dans *Continuité*, n. 29, Automne 1985, p. 45.
- Desautels, Louise "L'Hiver Québécois à la rescousse", dans *Québec Science*, Vol. 25 n. 9, Mai 1987.
- Gagné, Jean, "Le bateau sous le musée", dans *L'Escale*, Janvier-Février 1985, pp. 42,43.
- Grattan, D.W. McCawley, J.C., "The Potential of the Canadian Winter climate for the freeze-drying of degraded waterlogged wood" dans *Studies in Conservation*, Vol. 23, n.4, Novembre 1978.
- Grattan, D.W., McCawley, J.C., Cook, C. "The Potential of the Canadian Winter climate for the freeze-drying of degraded waterlogged wood", Part 11, dans *Studies in Conservation*, Vol. 25, n.3, Août 1983.
- La Roche, Daniel, "Pas un, mais plusieurs bateaux sous le musée", dans *L'Escale*, Mai-Juin 1985, pp. 18,19.
- La Roche, Daniel, "L'embarcation échouée à l'arrière de la maison Estèbe à Québec: un spécimen de transporteur léger au XVIIIe siècle", dans les actes du premier colloque international sur les traditions maritimes au Québec, Été 1985, pp. 410 à 416.
- Rémillard, Francine, "Objets de grandes dimensions en bois gorgé d'eau, techniques européennes de traitement et de mise en valeur" Rapport de mission, M.A.C., Novembre 1985, 58 p.
- Proceeding of the ICOM Waterlogged Wood Working Group Conference, Ottawa 1981.



## SUMMARY

This article gives a technical description of the stainless steel treatment tanks and auxiliary equipment for the conservation of waterlogged wood by the hot polyethylene glycol (PEG) method at the National Maritime Museum, Greenwich. The ventilation of the treatment area and the storage facilities for waterlogged material and used PEG solutions are also discussed.

# A LARGE SCALE POLYETHYLENE GLYCOL CONSERVATION FACILITY FOR WATERLOGGED WOOD AT THE NATIONAL MARITIME MUSEUM, GREENWICH

Richard W. Clarke & Christopher Gregson  
Conservation Division  
National Maritime Museum  
Greenwich, London SE10 9NF, England

## Introduction

A large scale facility for the conservation of waterlogged wood was seen as an important pre-requisite in the development, in 1970, of the Archaeological Research Centre at the National Maritime Museum, Greenwich. It was decided after consideration of the conservation techniques available at the time, to develop a system based on polyethylene glycol (PEG) impregnation by tank immersion. McGrail (1) describes the proposed layout of this conservation facility involving a flow-through system incorporating provision for wet wood storage, cleaning and recording areas, and treatment tanks. Due to various financial constraints however, some of these proposals have had to be modified. The number of treatment tanks has been reduced from four to three, admittedly with little change in total capacity ( $14.8\text{m}^3$  to  $13.7\text{m}^3$ ). The major part of the storage facilities for pre- and post-treatment material is centred at an external site some 4km distance from the museum. Modifications to the design of the building have also been necessary but these will not be discussed here.

The installation of the conservation facilities has progressed in phases over the last fourteen years. Tank 3 was in fact installed first and from the experience gained the specifications for Tanks 1 and 2 were developed. The system is now complete and operational and provides the largest permanent treatment capacity for the conservation of waterlogged wood using the hot PEG method in the U.K.

This paper describes the waterlogged wood conservation facility at the National Maritime Museum and provides a comparison with other tank impregnation systems described in the literature (2-11). It is not intended to present a design programme for other conservation centres. Instead, it is hoped that by adding to the general body of information the most efficient and economic facilities can be developed in any future installations.

## Treatment tank construction

The internal and overall dimensions for each treatment tank are shown in Table 1. All the tanks are constructed of 4.8mm (3/16" swg) mild steel lined with 1.6mm (1/16" swg) Type J stainless steel

	overall/ length	(internal) width	dim(m) depth	capacity ( $\text{m}^3$ )	no. of legs	no. of lids
TANK 1	2.1 (1.98)	1.7 (1.6)	1.1 (1.0)	3.17	6	3*
TANK 2	8.0 (7.88)	1.12 (1.0)	1.1 (1.0)	7.88	10	6**
TANK 3	3.6 (3.4)	1.0 (0.8)	1.1 (0.97)	2.64	6	3***

Table 1: The overall and internal dimensions and total capacities of the three stainless steel PEG treatment tanks at the National Maritime Museum. The number of support legs and lids for each tank is also shown.

(\* lids completely removable)

(\*\* lids hinged with pneumatic lifting system)

(\*\*\* lids hinged and fitted with support stays)



Figure 1: Tank 1 with a single lid removed. In the centre of the figure the resistance thermometer for the control of treatment solution temperature can be seen entering the tank. The junction box for the tank heating system can also be seen in the bottom left of the figure. (© NMM)



Figure 2: Tank 2 showing the single skin construction of the lids with support stay and the externally positioned polystyrene sheet insulation. The three control boxes for the tank heating system can be seen along the bottom edge of the tank. (© NMM)

(see Appendix 1) and are of welded construction; all welds tested for leaks using the Ardrex method (see Appendix 2). Stainless steel was chosen as the lining material because of its resistance to corrosion by hot, concentrated PEG solutions (12,13). The support legs are made of mild steel and each tank has a ground clearance of 19cm to allow for crane access and cleaning, and to minimise floor contact corrosion.

Tanks 1 and 2 are each fitted with two flush mounted 50mm diameter drain taps, incorporating Worcester ball type shut-off valves; one in the base of the tank to allow complete emptying and the removal of accumulated residues, and one positioned 40mm from the bottom of the tank to permit drainage, by gravity drain, to a low level. Tank 3 has a single flush mounted 50mm diameter drain tap, fitted with a shut-off valve, positioned 40mm from the bottom of the tank. Complete emptying and the removal of any residues from this tank has to be done by hand.

The base and sides of each tank are insulated with 50mm thick mineral wool slabs held in place by flanges within the tank structure and clad with 1.6mm (16g) mirror type finish stainless steel sheeting secured with self tapping screws.

The type of construction described above was found to be adequate for Tanks 1 and 3 but, during acceptance trials, proved unsuitable for Tank 2, the largest of the three tanks. The pressure of the water within the tank when full was sufficient to cause the sides to splay out such that the lids in the mid section of the tank could not be secured in the down position. It was therefore necessary to fit three internal 13mm diameter stainless steel braces across the top of the tank below the line of the lids. During loading and unloading of material these braces can be removed and then replaced when filling with, or draining off, water and/or PEG solutions. The braces are maintained in position throughout the treatment programme.

#### Tank lids

The number and arrangement of the lids for each tank is shown in Table 1. All the lids are of stainless steel construction and each is fitted with an adjustable ventilator to control the rate of evaporation from the tanks. The lids for Tank 1 (Fig.1) and Tank 2 are insulated with 25mm thick mineral wool slabs and clad with stainless steel sheeting secured with stainless steel self tapping screws. The lids for Tank 3 are made of a single sheet of stainless steel with folded edges to give rigidity and are insulated externally with loose fitting 45mm thick polystyrene sheet. Each lid is fitted with a stainless steel support stay to hold it in the open position (Fig.2).

The double stainless steel skin construction used for the lids of Tanks 1 and 2 resulted in them being very heavy and difficult to lift manually. This problem was exaggerated by the insulating material absorbing water vapour during the treatment phase. After a period of operational experience the system has been modified. For Tank 1 the insulating material has been removed and replaced with external loose fitting 45mm thick polystyrene sheet. Although making the lids lighter it still requires two people to remove them.

For Tank 2 a pneumatic lid lifting system is used (Fig.3). Compressed air, at approximately 7 bars (c 100psi), is provided by a Fluidair S2R 20 compressor. Each lid can be raised or lowered independently by means of a piston and pulley arrangement operated through individual control levers. The lids can be held in any position and when fully open are secured by a simple latch mechanism which can be released by hand with the operator standing clear of the lids.

The lids for Tanks 1 and 2 were designed so that their edges



should provide a self sealing joint when closed. This however was not the case in the final construction with the result that gaps of approximately 10mm were left between adjacent lids. This was particularly apparent with Tank 2. The gaps have been sealed using removable T-section stainless steel bars with neoprene strip beneath. The lids for Tank 3 have a good edge-to-edge seal.



Figure 3: The pneumatic lid lifting system for Tank 2 with the extraction hoods above. (© NMM)

#### Circulation system: pipework and pumps

A diagrammatic representation of the arrangement of valves and pipework for each tank is shown in Fig.4. All tanks are fitted with externally mounted stainless steel pipework for the circulation of PEG solution with isolating valves and flexible expansion joints on both the flow and return sides of the system. For Tanks 1 and 3 all pipework is of 40mm diameter; the inlet pipe enters the tank at high level and the outlet leaves at low level feeding direct into the inlet side of the circulation pump. The inlet and outlet points are at opposite ends of the tank. For Tank 2 the pipework is of 50mm diameter; the inlet pipe entering the tank at high level mid-way along its length. Outlet pipes are situated at low level at both ends of the tank and feed via a common branch into the inlet side of the circulation pump. All the pipework is of sectional construction, with lengths not exceeding 2m, joined by screw connections to facilitate dismantling and cleaning.

The inlet pipes are each fitted with a stainless steel spreader bar which can be positioned at high or low level within the tank. Each bar is drilled with 5mm diameter holes at 30mm centres. The outlet pipes are fitted with coarse drilled stainless steel filter heads to protect the pump rotors during the treatment phase.

All external pipework is insulated with 25mm thick sectional pipe insulation clad with light gauge shaped metal sheathing.

The circulation pumps (Fig.5) are of internal stainless steel construction mounted on a mild steel fabricated base plate and are of the positive rotary type working with flooded suction. Stainless steel trilobe rotors are used suitable for working at temperatures of up to 100°C and capable of pumping PEG solutions with a relative density of 1.2 and a viscosity of 10 poise maximum at 70°C. The pumps are fully reversible; the drive unit is connected to the pump shaft such that the speed of the pump can be regulated between zero and approximately 500rpm. All the electrical motors are fan cooled and rated at 415V/50Hz on a three phase supply. Each pump is fitted with a drain valve to allow the tanks to be emptied mechanically if necessary.

The pump for Tank 1 is a model 150 NDM/SHS/HJ (40mm) with a delivery of 118 litres min<sup>-1</sup> at 600rpm against a 1.5m head. The

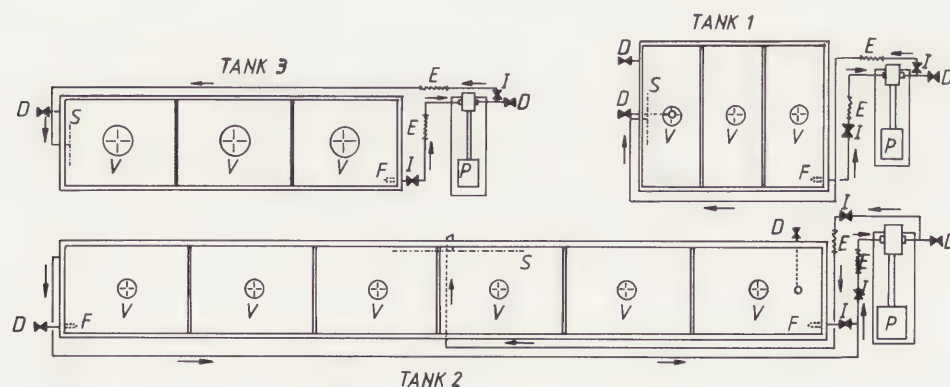


Figure 4: Diagrammatic representation of the circulation system, including the location of valves, for each of the three treatment tanks. D, drain valve; E, flexible expansion joint; F, filter head; I, isolation bar; P, pump; S, spreader bar; V, ventilator. Arrows indicate direction of circulation flow. (© NMM)

electric motor (Type 4EC, 2.2kW, 1410rpm) is mounted on top of a Carter size 14 hydrostatic infinitely variable speed drive unit. The pump for Tank 2, the largest of the three, is a model 200 ND/HJ/SHS (50mm) with a delivery of 227 litres  $\text{min}^{-1}$  at 550rpm against a 1.5m head. The electric motor (Type TEFC, 4kW, 1420rpm) is mounted on top of a Carter size 3A variable speed drive unit fitted with a No.5 SFRD Ritespeed gear box, ratio 2.33:1.

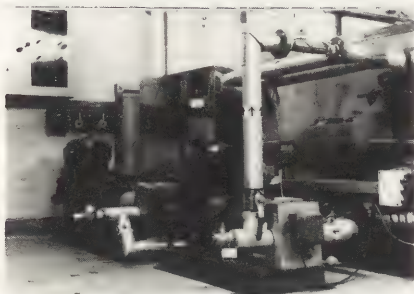


Figure 5: The circulation pumps for Tank 1 (foreground) and Tank 2 (background). The heating mantles for the pump heads are shown in position. (© NMM)

For Tank 3 the pump is a model 150 NDM/SHS (40mm) with a delivery of 45 - 90 litres  $\text{min}^{-1}$  at 450rpm against a 1.5m head. The electric motor is the same as for Tank 1 but mounted on top of a Carter size F13 variable speed drive unit fitted with a No.5 SFRD Ritespeed reduction gear box, ratio 3:1.

#### Tank heating system and temperature control equipment

All three treatment tanks are heated from beneath using mineral insulated, stainless steel sheathed heating elements mounted on a stainless steel mesh carrier. The heating elements for Tank 1 (Isopanel Type IPS-SS/EL-1.95) have a total loading of 6.25kW at 240V operating in three stages (i.e. 1.25, 2.5, and 6.25kW) and are contained in one panel comprising five interleaved circuits of 1.25kW each. For Tank 2 the heating elements (Isopanel Type IPS-SS/EL-1.75) have a total loading of 14kW at 240V again operating in three stages (i.e. 3.5, 7.0, and 14kW) contained in four heating panels of 3.5kW each with each panel comprising of four interleaved circuits of 875W respectively. Tank 3 has three interleaved heating panels (Isopanel Type IPS-3) each with a loading of 3kW at 240V.

All external pipework for Tanks 1 and 2 is heated using Isotape ITWSS-33 trace heating cable. For Tank 1 the cable has a loading of 275W at 240V and for Tank 2, a two section system with loadings of 615W and 325W at 240V respectively. Isotape ITX-6 trace heating cable with a loading of 60W at 240V is used for heating the external pipework of Tank 3.

Each of the three pump heads is fitted with a heating mantle to facilitate the flow of concentrated PEG solution through the pump rotors (Fig.5). For Tanks 1 and 3 an Isomantle IAW/150NDM (110W at 240V) is used and for Tank 2 an Isomantle IAW/200ND (130W at 240V) is fitted.

The heating circuits for Tanks 1 and 2 are switched through contactors and are wired in series or parallel to achieve the appropriate loading. Tank 1 has three 30A contactors working from a 240V single phase supply. Tank 2 also has three contactors, two 30A and one 40A, working from a 240V three phase supply, each contactor being connected to a separate phase.

The requirement for temperature control equipment was that treatment solutions should be able to be maintained at temperatures of up to  $60^{\circ}\text{C} \pm 1^{\circ}\text{C}$ .

For Tanks 1 and 2 treatment solution temperature is controlled by a resistance thermometer (PT 100DIN/L600) immersed in the liquid at a distance of 40cm from the base of the tank (Fig.1). The resistance thermometer has a platinum element housed in a stainless steel sheath. The signal from the thermometer is fed into a multi-regulating controller with a built-in set-point potentiometer. The output from the controller is then fed to a two stage switching relay connected, via the contactors, to the heating elements. The sensor controls the temperature of the tanks in two stages: at the steady state stages two and one (i.e. 2.5 and 1.25kW for Tank 1 and 7.0 and 3.5kW for Tank 2) are switched on and off according to the heat losses incurred.

When heating the tanks from cold or when additional heat is required the total heating capacity (stage three) of each tank



(i.e. 6.75kW for Tank 1 and 14kW for Tank 2) is used. Stage three heating in both Tanks 1 and 2 is controlled by a separate immersion thermostat, one in each of the two tanks, comprising a flexible probe protected by a polycarbonate sheathing. Connected to the contactors of stage three, the heating is switched off when a temperature of approximately 5°C below steady state has been reached.

The heating system for Tank 3 is also controlled in three stages but incorporates manual controllers using a three way switch with high, medium and low settings (Fig.2). Once the steady state temperature has been reached the controllers are turned to the low setting and the system is operated through a thermostat wired to a stainless steel sheathed resistance thermometer immersed in the liquid.

During operational trials for Tank 2 it was found that stage one heating alone (i.e. 3.5kW) was not sufficient to maintain a solution temperature of 60°C ± 1°C; large fluctuations in temperature were observed whilst waiting for the stage two heating to switch on and off. For this reason heating stages one and two were wired together such that the tank now has effectively a two stage rather than a three stage heating system.

The pipework trace heating systems and the heating mantles at the pump heads are each controlled by individual thermostats.

#### Temperature recording equipment

A Foster Cambridge P120L multi-point recorder provides a continuous paper record of the temperature within each tank. Stainless steel sheathed resistance thermometers, two to each tank, are used. The thermometers are of two lengths - 100cm and 51cm - such that the temperature can be recorded at two levels and any stratification effects highlighted. To date, no such stratification of temperature has been observed.

The resistance thermometers are inserted through holes drilled in the tank lids.

#### Ventilation and air extraction system

A Uniframe Air Handling Unit 300 supplies fresh air to the treatment area through four 305mm diameter multicone adjustable diffusers. The air is filtered at the intake point and can be heated by heater batteries (total capacity 45kW) if required. A Centex Centrifugal Roof Extract Unit Type C760 removes water vapour etc from above the treatment tanks through specially constructed extraction hoods (Fig.3), and also assists in creating a more acceptable working environment in the treatment area. The extraction hoods and associated ducting are manufactured from 1.6mm (16g) and 1.2mm (18g) galvanised mild steel respectively.

#### Timber storage facilities

Large timbers awaiting conservation are stored underwater in large capacity tanks. At present, two tanks with a total capacity of 67.5m<sup>3</sup> are available. One tank is of welded construction, measuring 15.2 x 2.13 x 1.15m overall and is lined with heavy duty butyl rubber sheet. The second tank is a Braithwaite sectional construction tank measuring 14.75 x 2.75 x 1.55m overall. The sectional panels have internal flanges which hinder the movement and stacking of material within the tank and it is also susceptible to rusting. Despite these problems this tank, acquired in 1974, has given good service.

Both tanks are emptied by submersible electric water pump and

filled by hosepipe from a 30mm internal diameter mains water supply.

A third water storage tank has recently been acquired and is sited adjacent to the treatment area. It is manufactured from glass reinforced plastic and measures 4.3 x 1.8 x 0.76m overall with a total capacity of 3.9m<sup>3</sup>. The tank has a flush mounted drain in its base and is filled direct from a 20mm internal diameter mains water supply.

All the storage tanks have a ground clearance of 19cm to facilitate crane access.

Due to the relocation of storage facilities during 1985 the two steel storage tanks described above are to be replaced with ones constructed of glass reinforced plastic with a total capacity of 75m<sup>3</sup>.

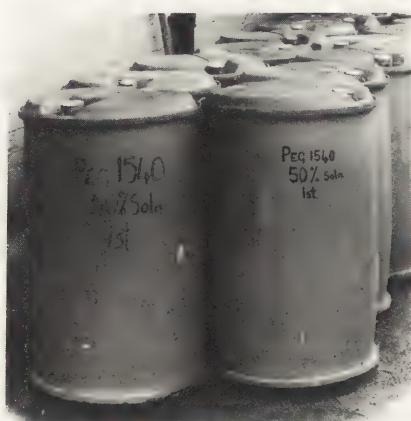


Figure 6: The barrel storage system for used polyethylene glycol treatment solution. (© NMM)

#### Storage of used treatment solutions

For reasons of economy it is intended to reuse PEG treatment solutions at least three times. At first it was envisaged that large capacity, heated stainless steel storage tanks would be used but the availability of space and finance dictated otherwise. The alternative has been to use 250 litre plastic Mauser L-ring drums (Fig.6). Used PEG solution (primarily PEG 1500) is transferred from the treatment tanks to the drums either by hand pump or via the drain valves on the circulation pumps; sufficient water and PEG solution is added to achieve a final concentration of 50% w/v PEG in each drum. Individual drums can be returned to the treatment area for the addition of PEG solution to the treatment tanks, metered by hand pump, during subsequent conservation programmes.

#### Conclusions

The conservation facility described above provides for the largest permanent treatment capacity for waterlogged wood using the hot PEG impregnation tank immersion technique in the U.K. A number of design faults have been commented upon but there have been no serious running problems since the tanks have been in operation. It is appreciated that more economical construction materials are available but these are primarily for short term use. It is intended that the installation described here should be capable of running for prolonged periods over many years. Such long term durability still needs to be evaluated of course but the indications are that the equipment should prove satisfactory.

#### Appendix 1 : The composition of Type J stainless steel:

The stainless steel is EN58J to BS970, Part 4, 1970. The current specification being 316 S16 BS1449, Part 2, 1975.

Constituents	Min. %.	Max. %.
Chromium	16.5	18.5
Nickel	10.0	13.0
Manganese	0.5	2.0
Carbon	0.07	0.2
Phosphorous	-	0.45
Sulphur	-	0.003
Silicon	0.2	1.0
Molybdenum	2.2	3.0

#### Appendix 2 : The Ardrox test method:

The Ardrox test method is a proprietary non-destructive test in which a red penetrating dye is sprayed onto the metal surface; a solvent being used to remove any excess. The surface is then treated with a developer solution; any cracks being revealed as bright white lines.

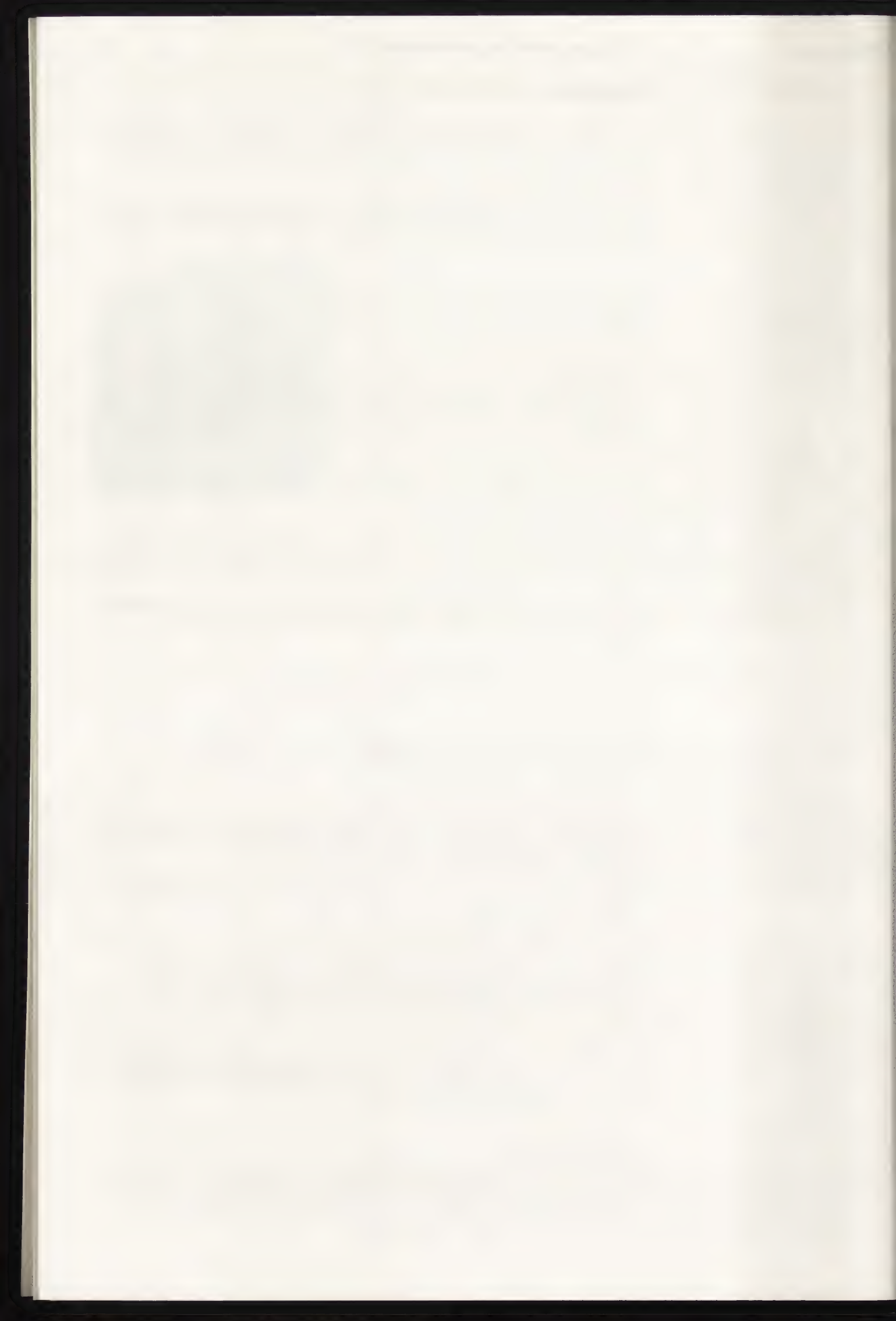


### References

1. McGrail, S. "Progress towards a centre for the conservation of waterlogged wood." In Problems of the Conservation of Waterlogged Wood, edited by W.A. Oddy. Maritime Monographs and Reports No.16, Greenwich, London, 1975: 107-8.
2. Christensen, B.B. The Conservation of Waterlogged Wood in the National Museum of Denmark. Studies in Museum Technology 1, The National Museum of Denmark, Copenhagen, 1970 .
3. Suthers, S. "The treatment of waterlogged oak timbers from Ferriby boat III using polyethylene glycol." In Problems of the Conservation of Waterlogged Wood, edited by W.A. Oddy. Maritime Monographs and Reports No.16, Greenwich, London, 1975: 115-9.
4. Grosso, G.H. "Volume processing of waterlogged wood at a remote archaeological site: Modifications of old techniques, identification of special problems, and hopes for their solution." In Pacific Northwest Wet Site Wood Conservation Conference Volume 1, edited by G.H. Grosso. Neah Bay, Washington, U.S.A., 1976: 35-48.
5. Alagna, P. "The construction of tanks used in the conservation of the wood of the Marsala Punic Ship." Studies in Conservation 22 (1977): 158-60.
6. Coles, J.M.; and Orme, B.J. "Conservation of wooden artifacts from the Somerset Levels: 1." Somerset Levels Papers No.3 (1977): 87-9.
7. Murdock, L.D. "A stainless steel polyethylene glycol treatment tank for the conservation of waterlogged wood." Studies in Conservation 23 (1978): 69-75.
8. Coles, J.M. "Conservation of wooden artifacts from the Somerset Levels: 2." Somerset Levels Papers No.5 (1979): 32-43.
9. Bryce, T. "The acetone rosin treatment of wood at the National Museum of Antiquities." In The Laboratories of the National Museum of Antiquities of Scotland, edited by T. Bryce and J. Tate, National Museum of Antiquities of Scotland, Edinburgh, 1980: 13-20.
10. Singley, K.R. "Design of a large scale PEG treatment facility for the Brown's Ferry vessel." In ICOM Committee for Conservation 6th Triennial Meeting, Ottawa, 1981: paper 81/7/5.
11. De Witte, E.; Terfve, A.; and Vynkier, J. "The consolidation of the waterlogged wood from the Gallo-Roman boats of Pommereul." Studies in Conservation 29 (1984): 77-83
12. Blackshaw, S.M. "Comparison of different makes of PEG and results on corrosion testing of metals in PEG solutions." In Problems of the Conservation of Waterlogged Wood, edited by W.A. Oddy. Maritime Monographs and Reports No.16, Greenwich, London, 1975: 51-8.
13. Barkman, L.G.; Bengtsson, S.; Hafors, B.; and Lundvall, B. "Processing of waterlogged wood." In Pacific Northwest Wet Site Wood Conservation Conference Volume 1, edited by G.H. Grosso. Neah Bay, Washington, U.S.A., 1976: 17-24.

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## SUMMARY

Archaeological wood found in moist soil and then dried is usually much degraded and unstable. When choosing the technique for its consolidation, the state of the wood, the size of the object and the available technical means are taken into consideration. In the Hermitage a dug-out boat (9th century) found in Volgograd region, some objects from Fergana (2nd-4th century) and some other objects have been successfully conserved with low viscosity polybutyl methacrylate solutions. In field conditions, to preserve the surface and slow down the drying, the wet degraded wood is secured with gauze bandages soaked in this polymer in acetone-xylene solution. After drying, the object is released from the bandages and is further consolidated with the polymer solutions. A comparative study of impregnation methods for much degraded dry archaeological wood with polymer solutions and wax-resin mixtures showed some definite advantages of the latter.

## CONSOLIDATION OF DRIED ARCHAEOLOGICAL WOOD

N.G. Gerassimova, K.F. Nikitina, T.A. Baranova, and E.P. Mel'nikova  
The State Hermitage Museum  
191065 Leningrad  
USSR

Wet or moist archaeological wood which has dried naturally, or rather slowly (e.g. without freeze-drying, or replacement of water in the wood by organic solvents) is referred to as "dried." The state of preservation of such wood largely depends on the extent of the oxidative, hydrolytic and biological degradation processes which have taken place. These processes are mainly the result of the conditions to which the object was exposed in the earth. The chemical composition of archaeological wooden objects buried in permafrost from the Pazyryk (USSR) mounds has been studied (1). It was found to have changed in composition only slightly. Equally old wood (ca. 3000 years) from peat-bogs, however, lost a considerable part of its carbohydrate content. Still greater changes, up to nearly complete destruction of carbohydrates, is observed in wood from earth mounds, especially near burial places. Here the important factors, as expected, are biological processes. That is why dried archaeological wood is a strongly lignified material, in which the lignin has been oxidised and destroyed to a considerable extent. Such wood is 2 - 3 times as light as sound wood, and has practically no mechanical strength along and across the fibres. Unlike wet wood, all voids and cavities in it are filled with air and wood dust and this hampers the entry of treatment solutions. Treatment with aqueous solutions may prove disastrous for such objects. The ability of some organic solvents to alter the lignin has also to be taken into account.

Judging by outward appearance, we divide dried archaeological wood into two groups: intermediate preservation, with a relatively dense, rough-wood like surface; and poor preservation, readily disintegrating, with a smooth surface which leaves dust on the fingers.

The choices of the conservation method for dry depends on state of preservation and size. The optimum method must not only stabilize the wood surface but also consolidate the whole structure. This means that the object should suffer no damage by action of its own weight and that it should be possible to glue up the fragments. The treatment must reduce the hygroscopicity of the wood and stabilize it to survive temperature and humidity fluctuations. It should increase the bio-stability and fire-resistance. It is preferable that the treatment be reversible and pose little toxic hazard.

In our routine work, impregnation with polymer solutions and with wax-resin compositions is used for conserving dry archaeological wood.



Figure 1. A wooden sculpture (woman idol), 9th century. Ashai expedition, Volgograd region. Excavations in 1975.



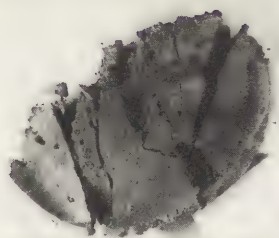


Figure 3. A wooden hollow dish, 2nd-4th century. Sufan burial-place, Fergana. Excavations in 1982. Before restoration.

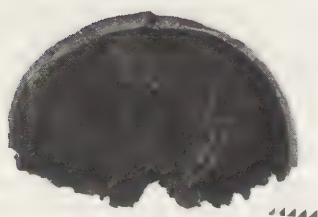


Figure 4. Dish (shown in Figure 3), after restoration.

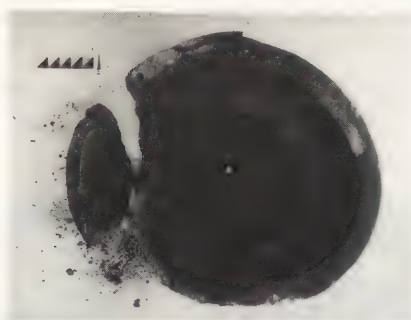


Figure 5. A bowl from Sufan burial place, 2nd-4th century. Before restoration.

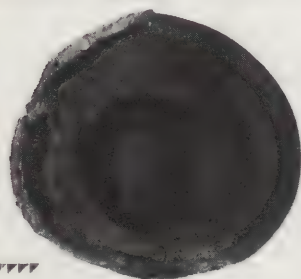


Figure 6. Bowl (shown in Figure 5), after restoration.



Figure 2. The sculpture (shown in Figure 1) glued up with bandages and put into a box with sawdust for transportation.

In 1961, on a sandy bank near the village of Mikhajlovskoye in the Volgograd region, an oak dug-out dating from the 9th century, was found by schoolchildren. As found, the wood of the boat had been wet, but for two months before it came under the care of the Hermitage, it had been drying. The preservation of the wood was estimated as intermediate but the overall condition of the boat was poor. The wood had warped, deep cracks had formed and some fragments had fallen out. Because of the large size of the boat (length 8 m, width and depth about 80 cm) and because it was necessary to conserve it on the spot, it was decided to impregnate it with low viscosity polybutyl methacrylate, (PBMA - LV) in xylene solution. The concentration varied from 5 to 15%. The next stage of treatment, assembling the fragments and applying putty, took place in the Hermitage. The restored boat is on exhibition in a glass-case and has been satisfactory up to now.

We have found that it is possible to preserve archaeological objects of wet degraded wood by securing them in the field with gauze bandages soaked in a 15 - 20% PBMA - LV solution in a 1:1 xylene-acetone. Bandaging this preserves the shape and crumbling surfaces, and retards the evaporation of the moisture. It also gives more safety to the object during transportation. In this way we preserved a 9th century wooden sculpture. This sculpture which depicted a female idol was also found in the Volgograd region in 1975. (Expedition of the USSR Academy of Sciences Institute of Archaeology Leningrad branch, under the guidance of V.P. Shilov.) The statue, carved from a whole oak trunk, is 158 cm high, and up to 55 cm wide. It stood in moist sandy soil at the foot of a mound and was surrounded by sheep and horse skulls. The statue was bandaged with gauze soaked in PBMA - LV/Acetone solution in the field. It was then packed in a box with sawdust. It was brought thus to the Hermitage Laboratory for Conservation of Organic Materials. Similarly, the 1982/83 state Hermitage Archaeological expedition to Fergana obtained some small tables, a bowl and a poorly preserved dish. They were found in the "Sufan" burial place and dated to the 2nd-4th century. For bandaging, PBMA - LV solutions in xylene-acetone mixtures were used. Later, in laboratory conditions they were released from the bandages and further impregnated with PBMA - LV in xylene. As the objects are small (the largest is 37 cm in length and up to 1.5 cm in thickness) this treatment gave satisfactory consolidation. The fragments of the objects were successfully glued up and the losses filled with putty.

The subsequent conservation of the idol was a matter for special discussion. Its wood was in a poor state, its size rather large and there was a display problem. The wood is brittle, in some places exfoliating and it produces dust. There are some cracks and voids. The wood density is about 400 kg/m<sup>3</sup> (the density of sound oak is 690 kg/m<sup>3</sup>). The chemical composition of the statue's wood indicates strong degradation. The lignin content approaches 60%, 2.5 times that for normal oak; the cellulose content (25%) is nearly twice as low. The wood of the idol is very sensitive to water and becomes limp in it. Because of the poor state of preservation, a number of experiments were conducted to select some means of consolidation. Experimental material was available from some oak



in a similar state found near the statue. We also used some samples of dry, very degraded archaeological fir of unknown origin. The lignin content was the same as that in the experimental material and the cellulose content was about 10%. Because of the nature of the wood and the lack of sufficient material, test samples were small and irregularly shaped. The impregnation depth, strengthening and decrease of brittleness were estimated by feel, after the samples had been sawn up across the fibres. Before weighing (before and after treatment) the wood was conditioned at a relative humidity of 45% and room temperature. The amount of the impregnant introduced into the wood was estimated by the weight increase. The hygroscopicity of the untreated and the treated samples was estimated by the change of the weight after the samples were kept in a chamber at a relative humidity of 95%. The hygroscopicity of the samples before treatment, thus determined was 11% for oak and 7.6% for fir.

Some soluble thermoplastic polymers capable of being dissolved out (thus giving the process reversibility) were tested as consolidants. These were: PBMA - LV, two grades of butyl methacrylate/methyl methacrylate copolymer, butyl methacrylate/octyl methacrylate copolymer, and butyl methacrylate/2-ethyl hexylacrylate copolymer. The viscosity indices of these polymers were close to that of PBMA - LV. They were used mainly as 20% solutions in xylene, acetone and methyl-ethyl ketone. Tested also were 10% solutions of polymethylsiloxane resin KO-921 in a 4:1 xylene-toluene mixture, alcohol solutions of some grades of polyvinyl acetate, polyvinyl butyral and ocypropyl cellulose. The polymer solutions were introduced with a brush. In addition, wax-resin compositions containing beeswax, waxlike polycaprolactone, pine rosin and laboratory samples of modified rosins were tested. The impregnation of the latter was carried out with the melted resins at a temperature of about 110°C. Some attempts were also made to apply concentrated solutions of polycaprolactone in combination with polymers in methyl-ethyl ketone solution.

The results of the work with polymer solutions showed that alcohol solutions swell the degraded wood. Shrinkage then follows which leads to exfoliation along the fibres. The xylene solutions also affected the degraded wood: they cause deformation of its structure, by probably acting upon the lignin. The best results were obtained with solutions of methacrylate polymers in methyl-ethyl ketone. Because the experimental material was scanty and non-uniform, and because the use of brushes gives variable impregnation, the data obtained were scattered. It did not permit analysis the results to be carried out with certainty. The polymer content in the treated fir and oak samples varied from 18% to 55% (based on the mass of air dry samples before treatment). The decrease in hygroscopicity in oak varied from 1.9% to 4.8% and in fir from 1.9% to 3.7%. In all cases the polymers did not consolidate the wood sufficiently, which remained brittle and tended to exfoliate easily.

In comparison to the polymer solutions, the wax-resin compositions have definite advantages as impregnants. Firstly, no flammable or toxic solvents were used. Secondly, the melted resins filled all the cavities and voids of the destroyed wood and on cooling supported and glued the weakened cell structure. They also cemented together the exfoliated fibres. After treatment with molten beeswax and pine rosin (1:1 by weight) the weight increase was 245% in oak and 155% in fir. The decrease in hygroscopicity was 7.9% and 6.1% respectively. Modified rosin (4 samples) in analogous mixtures with wax showed similar weight increases with a smaller decrease in hygroscopicity.

For the conservation of the idol we consider it possible to use impregnation with a wax-rosin mixture using the Plenderleith and Werner method. We have already used it for conserving objects, including large objects of dry wood from archaeological excavations. For example, in this way, the larch cover of a coffin from Bashadar (Altai, 6th century B.C.) was treated. The treatment of the idol is not yet completed as in situ radiation polymerization of monomer is being discussed as an alternative.

#### References

1. Zaitseva G.I., Obolenskaya A.V., Leonovich A.A. et al., "Studies on the dependence of the degree of degradation of archaeological wood upon the duration and conditions of burial." From *Kratkiye tezisy dokladov Vsesoyuznogo seminara "Novyye metody issledovaniya, konservatsii i restovratsii khudozhestvennykh proizvedenij (polevaya i laboratornaya konservatsiya pamyatnikov arkheologii)*, Leningrad, 1985, p. 62-63.
2. Plenderleith H.J., Werner A.E.A. The Conservation of Antiquities and Works of Art. 2nd ed., London, 1971, p. 136.





## SUMMARY

We studied the conservation of waterlogged oak /with bark intact/ dating from the 16th century. Stabilization was achieved with an unheated sucrose solution. The concentration of the solution was increased step by step. The wood remained in this solution long enough to guarantee total sucrose penetration and equal dispersion throughout.

The best results were obtained for the samples which were soaked for 5 months. 85% ASE was achieved, and the colour and appearance were natural.

Scanning electron microscopical /SEM/ studies showed that the vessels and fiber cells were deformed in the non and badly conserved dry samples. The samples, well conserved with sucrose solution kept their original sizes. The sucrose fills the cavities of fiber cells but leaves the vessels empty.

According to our experiments, sucrose gives a good result and is an inexpensive treatment easy to carry out.

The article includes a literature review of sucrose treatments.

## THE CHEAPEST METHOD FOR CONSERVATION OF WATERLOGGED WOOD: THE USE OF UNHEATED SUCROSE SOLUTIONS

András Morgós

Chemical engineer, restorer

National Centre of Museums, Restoration Department

H-1087 Budapest, Könyves Kálmán krt. 40

Lucia Glattfelder-McQuirk

restorer

Archaeological Institute of the Hungarian Academy of Sciences

H-1250. Budapest, Uri u.49

Erzsébet Gondár

chemist

Innovatext Textile Engineering

H-1103. Budapest, Gyömrői ut 86

### 1. Introduction

Archaeological waterlogged wood is destroyed whether buried in the soil or immersed in water over a long period. If such wood dries without treatment, it shrinks irreversibly and warps. To restore the original size is impossible. The aim of conserving such wooden objects is to maintain the dimensions and shape of the wood as waterlogged.

The conservation of waterlogged wood can be divided into two main categories. In the first the water is removed from the wood in such a way that the structure does not collapse. Methods such as solvent exchange or freeze-drying are examples. The water-free wood is then impregnated with a non-aqueous resin solution /e.g: acetone-resin, alcohol-ether-resin, methyl methacrylate monomer/.

In the second category the waterlogged wood is treated with water soluble consolidants such as polyethylene-glycols, urea-formaldehyde, melamine-formaldehyde prepolymers or the formerly used alum. The final stage is controlled air drying or freeze-drying.

The economics of treatment are determined by the price of the chemicals, the cost of heating of the conservation liquid, and the capital expense of complicated equipment. Conserving large objects is particularly expensive.

In choosing the conservation treatment we must take into consideration the fire, explosion, and health hazards of the chemicals used.

Considering these problems, we tried to select and then test a method which minimizes the cost and hazards.

For this we set up the following criteria:

- the conservation must use an inexpensive material available in every country
- the conservation liquid should not be heated during the long conservation period
- special equipment should not be required
- the chemicals used should not be a fire, explosion, or health hazard.

These criteria were satisfied with a sucrose-based treatment.

### 2. Impregnation of wood with sucrose - a literature review

The impregnation and stabilization of wood with sucrose is a method which has been studied for many years.

In 1903 in a German patent /1/, and later in 1904 in an American /2/ one, Powell described the strengthening of wood with a sucrose-solution and observed that the treatment improved the dimensional stability of wood. The treatment fills cellular cavities, thereby decreasing shrinkage.

Stamm /3/ also improved dimensional stability significantly with sucrose-solutions. His results for maple and birch are summarized in Table 1.

Table 1.

Stamm's results treating wood with sucrose solution			
Type of wood	Impregnation liquid	Absorbed sucrose / % /	Reduction in shrinkage / % /
maple	30% sucrose solution	41	82
	17% sucrose solution	29	62
	9% sucrose solution	27	50
	concentrated molasses	51	85
	half concentrated molasses	39	65
birch	30% sucrose solution	36	72
	17% sucrose solution	26	58
	9% sucrose solution	13	33
	concentrated molasses	63	78
	half concentrated molasses	49	72

During the impregnation, the hygroscopicity of the wood only changes slightly. The dimensional change of treated wood is effectively controlled between 50-100% relative humidity. Impregnating with a 50% sucrose solution decreases the shrinkage by 88%. Stamm noted, that sucrose contains almost all of the ideal qualities to be a good bulking agent for wood. It is non-corrosive, non-volatile, non-toxic, and very soluble in water.

Gratchev and Kovalenkov /4/ impregnated the wood with unrefined sugar and potato molasses at a 100C and 140C. As a result compressive strength increased considerably: the change in size decreased by 40% for treated Scotch pine and European pine and 50% for treated birch.

Experiments by Tiemann using a 42% w/v sugar/solution /5/ showed that sugar readily penetrated the sapwood of most species, the heartwood of a few and reduced the shrinkage and swelling of the treated wood. He found the best results using crystalline cane sugar. In a humid environment molasses or invert sugars can leave the wood feeling damp and sticky.

Because of the solubility of absorbed sugar, wood so treated is unsuitable for outside applications.

Since sugar can be dissolved out of treated wood, the treatment is reversible.

For industrial purposes, the solubility of glucose in birch /treated by a 2% solution/ is reduced by a heat-pressure process. This takes place at 160C and extends for 3h. /6/ Dimensional stability is thus increased by 71-74% and hygroscopicity by 9,5%. During the treatment the glucose forms oxymethyl-furfural, methyl-furfural, and formaldehyde.

Conservation of waterlogged wood with sucrose-solutions, according to our knowledge, was accomplished first by Soviet researchers in Minsk /7,8/. Unfortunately, their publications are only available with difficulty. In the German Democratic Republic the Minsk process has been used for some time. It is uncertain whether this is the same as the above treatment or a variation of it. In the latter process the waterlogged wood is placed in a 50% o-hydroxy-benzylalcohol solution at room temperature for 30 min. Subsequently it is immersed in a boiling 1:1 sucrose water solution of which the pH is controlled with lactic acid to between 3-4. This treatment is repeated 6 times and the impregnation time is increased by 5 min. each time. Finally the wood is boiled for 60-80 min. until the wood sinks. After removing the wood from the solution it is washed with hot water and finally left to dry in the air.

Barkman and his co-workers /9/ compared the sucrose, sodium chloride, and PEG 1000 treatments. They concluded that the sucrose gave least shrinkage; 85% ASE.\*

Usually a conservation method's ASE-value must be over 75%. /10/ The use of sucrose to treat waterlogged wood is mentioned by McCawley. /11/

Grosso described /12/ and experimental application of the sucrose method of conserving waterlogged wood using a 40% /v/v/ solution.

\* An ASE of 100% means that the wood on drying keeps the swollen or waterlogged dimension.

ASE = Anti-Shrink-Efficiency

ASE % =  $\frac{\text{Original shrinkage} - \text{Shrinkage of treated wood}}{\text{Original shrinkage}} \cdot 100$



Results are reported on the effects of several biocides in the sugar solution. Growth of organisms in and on the test solutions is described. Superior results were noted with ascorbic acid. Comparison of results of sucrose with the polyethylene glycol Carbowax 540 Blend is given.

Grattan /13/ at the ICOM Committee for Conservation Meeting in Copenhagen in 1984 mentioned sucrose treatments: "Sugars as alternatives to PEG are gaining increasing use as impregnants and pre-treatment freeze-drying". He mentioned that Useful work on sucrose was carried out by Parrent in Texas U.S.A. and Grosso in Washington State U.S.A. /12, 14/ Mannitol was studied by Barbour in Seattle Washington State U.S.A. and by Murray in Portsmouth, /18/ England. Grattan and Cook at the Canadian Conservation Institute in Ottawa, Canada studied sorbitol in comparison to the above sugars. /19/

Extensive studies by Parrent /14, 15, 16/ demonstrate that sucrose treatment is a reliable method for conserving waterlogged wood. An overall antishrink efficiency of 87% was achieved and the resulting appearance is aesthetically pleasing.

The treatment of Parrent /16/ used solutions starting at 5% sucrose /w/v/ at room temperature. After immersion of the wood samples, the temperature was gradually increased 50C and held steady for the duration of the treatment. At two-week intervals the sucrose concentration was increased by 5% increments until a 45% solution was obtained. The wood was held in this solution until it reached equilibrium as determined by the cessation of weight gain of the wood. The solutions were then increased every two weeks by 10% increments until 100% sucrose was obtained. After two weeks in the solution the wood was removed and allowed to dry in the air.

Light and scanning electron microscopical photographs show conclusively that sucrose penetrated the ultrastructure of the wood and bulked it to prevent collapse of the fiber cells, vessels and other voids in the wood.

The reversibility of the sugar treatment was tested by soaking a wood sample treated with sugar. The sugar dissolved readily out of the wood. The linear decrease in hygroscopicity of the treated wood as the sugar content increases supports hydrogen bonding between the hydroxyl groups of the sucrose and the cellulose of the wood.

### 3. Sucrose and it's characteristics

Sugars according to their chemical constructions are mono and oligosaccharides. Among the great numbers of these compounds only a few of them have practical importance. The following Table /2/ gives some information about their composition and origin:

Table 2.

Frequent sucrose-types and their origins

Sugar-type	Monosaccharide units		
	Names	in numbers	present in
sucrose	D-glucose and D-fructose	2	sugar beet sugar cane
maltose	D-glucose and D-glucose	2	barley
lactose	D-glucose and D-galactose	2	milk
glucose	D-glucose	1	honey, grape
raffinose	D-glucose and D-galactose and D fructose	3	beet molasses

Sucrose is a disaccharide produced from sugar-beet or sugar-cane. It is comprised of D-glucose and D fructose units. It dissolves in water easily, but is practically insoluble in alcohol and ether. It's solubility in water is shown in Table 3.

It forms colourless, monoclinic crystals and has a molecular weight of 342,3 a melting point of 170-186C, and a density of 1,588.

Chemical formula:  $C_{12}H_{22}O_{11}$

Structural formula:

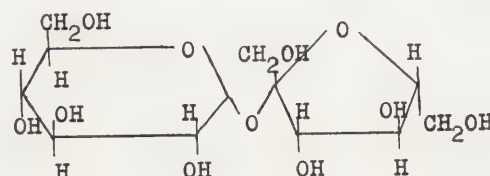


Table 3. Solubility of cane /or beet/ sugar in water /17/

Temp. °C.	Per cent sugar	Grams of sugar in 100g H <sub>2</sub> O
0	64.18	179.2
5	64.87	184.7
10	65.58	190.5
15	66.33	197.0
20	67.09	203.9
25	67.89	211.4
30	68.80	219.5
35	69.55	228.4
40	70.42	238.1
45	71.32	248.7

Temp. °C.	Per cent sugar	Grams of sugar in 100g H <sub>2</sub> O
50	72.25	260.4
55	73.20	273.1
60	74.18	287.3
65	75.88	315.0
70	76.22	320.4
75	77.27	339.9
80	78.36	362.1
85	79.46	386.9
90	80.61	415.7
95	81.77	448.5
100	82.97	487.2

#### 4. Experiments and conservation method applied

A waterlogged oak branch found among other wooden-objects in a 16th century well, was used in these experiments. Average water-content was 414%, oven dry /103C/ weight basis. The experimental samples were about 5 cm in diameter.

From the results of previous experiments we determined the treatment conditions. The conservation was done in the following way:

We put the waterlogged wood into a 50 g/l sucrose solution in water. The concentration of the solution was given in g sucrose/ l water, because addition of more sucrose alters the total volume of the bath. The quantity of water in the samples was ignored, because this was negligible compared to the water volume of the bath.

To prepare the conservation solution we used crystalline beet sugar. The quality of this is defined by the Hungarian Standard No. 3671. The sugar used contained 99.75% sucrose, determined by polarimeter, maximum moisture content 0.10% and insoluble matter context max. 50mg/kg.

The impregnation solution contained 1% /w/v/ sodium-pentachlorophenol to prevent growth of microorganisms. The bath was kept at room temperature during the whole conservation period. Every 2 or 3 days the concentration was raised by 50 g/l sugar. After 40 days it reached 750 g/l. Thereafter we continued to put the sugar into the bath in 50 g/l portions, but we waited until previously added sugar dissolved. Stirring was not necessary. After another 30 days we reached the final sugar water concentration, 1050 g/l.

The quantity of sucrose absorbed and the ASE values are shown in Table 4/.

The best results were shown in the samples which were impregnated for 5 months. These samples not only kept their form, but the bark remained intact as well. Other samples, which were impregnated for 1 or 2 months only, cracked quite strongly and shrank in the radial and tangential directions. The results are shown in Figure 1.

The samples were dried under sand for 23 days, then in air. 5 cm diameter samples needed about 70 days to reach constant weight. indicated in Figure 3.

Table 4. The sucrose absorption and ASE values of the treated oak wood during different time of the conservation

Time of conservation	1 month	2 months	5 months
Concentration of the sucrose-solution/g sucrose/ l water/	550	950	1050 <sup>x</sup>
The absorbed sucrose content of the wood after air drying %/ <sup>xx</sup>	265.3	388.1	473.8
ASE-values %/ <sup>xxx</sup>	66	76	85

<sup>x</sup> -the final concentration was reached in 70 days, then the wood was kept in this solution

<sup>xx</sup> -the % sucrose absorbed was calculated on the basis the oven /103C/ dry wood

<sup>xxx</sup> -ASE value was calculated from the diameter change of the wood sample

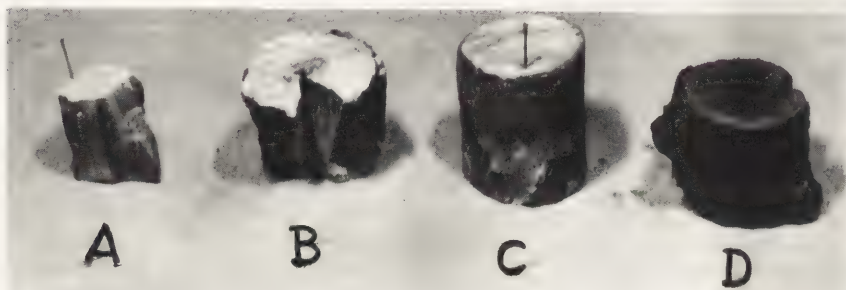


Figure 1. The unconserved and the treated waterlogged oak samples. All were cut from the same branch. A- air dried, without conservation; B- impregnated for 1 month; C- impregnated for 5 months; D- unconserved wood in waterlogged condition



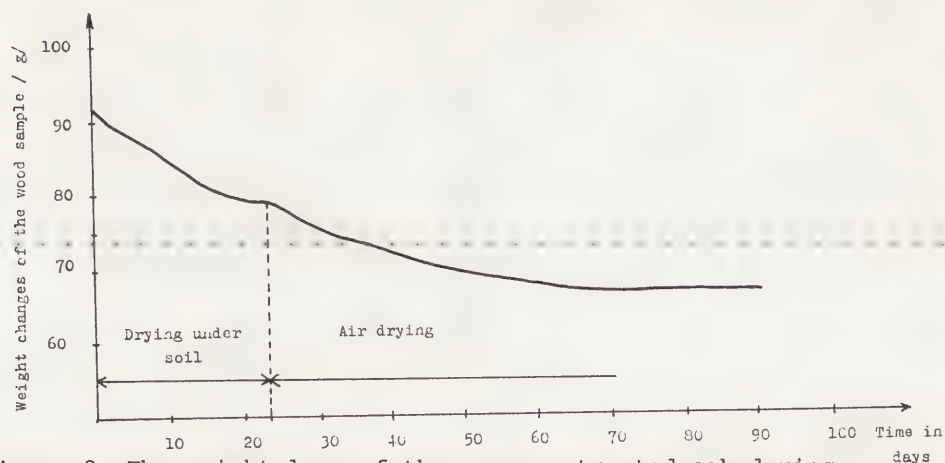


Figure 2. The weight loss of the sucrose treated oak during drying. The sample was impregnated for 5 months. See Fig. 1., sample C.

### 5. Scanning electron microscopical studies

We took scanning electron microscopical photographs through the samples shown on Figure 1. Results are shown in Figs. 3-8.

To demonstrate dimensional change the air dried, the unsatisfactorily conserved and the well conserved samples, the earlywood vessels and fiber cells are shown in Figs. 3,5,7 at identical magnifications. For well preserved wood in Fig. 7, deformation cannot be seen. The cross-sections of vessels /V/ are almost round, the fiber cells /F/ show normal hexagonal forms. In the case of the unsatisfactorily conserved and air-dried, unconserved samples, the vessels and fiber cells are seen to have lost their normal forms. Under stronger magnifications this can be seen more clearly /Figs. 4,6/. The vessels shrink to a higher degree in the tangential direction and that is why, the normal round cross-section of the vessel is deformed in the radial direction and becomes elliptical. For the well conserved wood /e.g. with sucrose/ sucrose fills the fiber cells almost totally, while it leaves the vessels' large lumina empty. /Figs. 7,8/ The vessels have probably been reinforced by a thin layer of sucrose adhering to them. For the unsatisfactorily conserved wood /Figs. 5,6/ the sucrose fills the fiber cells only partially. Obviously this is not enough to preserve the wood from deformation.

### 6. Conclusions

The advantages of the sucrose conservation method are summarized as follows:

1. Because of its small molecular weight, sucrose diffuses readily into the wood. Molecular size is in the same range of that of PEG 300-400. Because of its small molecular size it can also penetrate into the cell walls.
2. The sucrose molecule which penetrates into the cell wall is able to hydrogen bond with the cellulose molecules of the wood and also with the decomposition products.
3. The treated wood is non-hygroscopic, unlike wood treated with low molecular weight PEG.
4. The crystallized sucrose has a high stability, that is why it consolidates the wood very well.
5. The conservation is cheap, simple and doesn't need special equipment.
6. Wood can be impregnated without heating and the sucrose very easily dissolves at room temperature.
7. The treatment has no fire, explosive or health hazards except for those caused by antimicrobial agents.
8. Sucrose is not corrosive, does not evaporate and is easily obtainable and cheap.
9. Sucrose increases dimensional stability of wood in fluctuating relative humidity.
10. After treatment the wood keeps its natural colour and can be glued with the most adhesives.

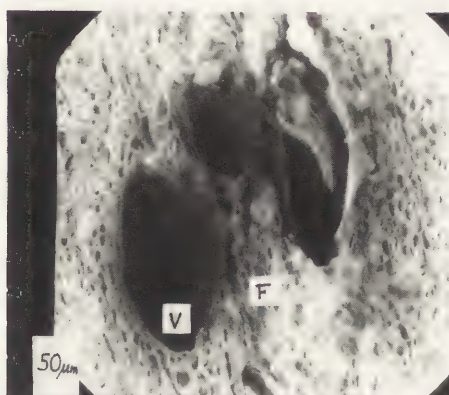


Figure 3.

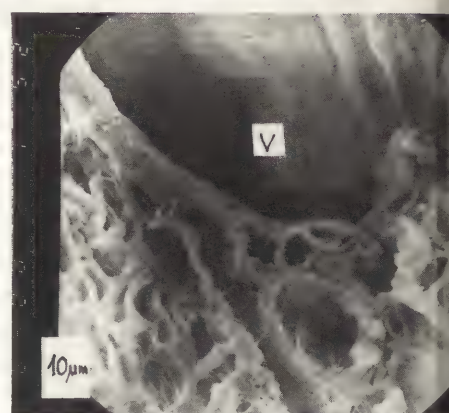


Figure 4.

Figures 3. and 4. Scanning electron micrograph of air-dried, unconserved waterlogged oak, transverse plane, showing considerably collapsed earlywood vessels /V/ and fiber cells /F/. The micrograph was taken from the sample A, see Fig.1.

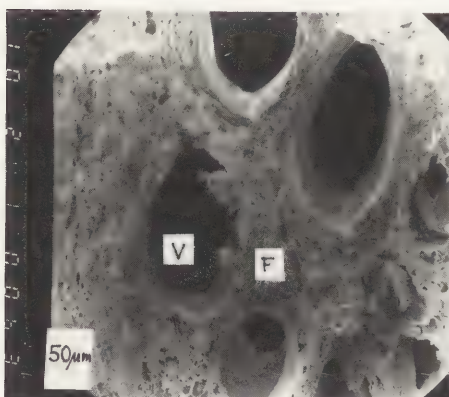


Figure 5.

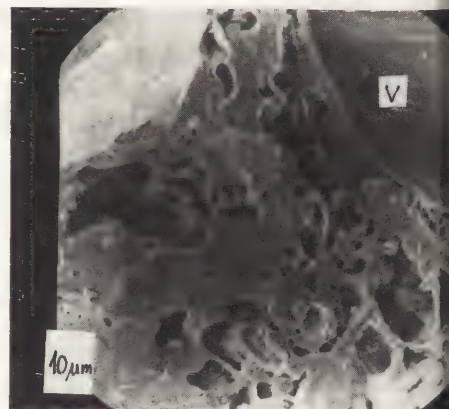


Figure 6.

Figures 5. and 6. Scanning electron micrograph of waterlogged oak unsatisfactorily conserved with sucrose, transverse plane, showing collapsed vessels /V/ and fiber cells /F/. The micrograph was taken of sample B in Fig. 1.

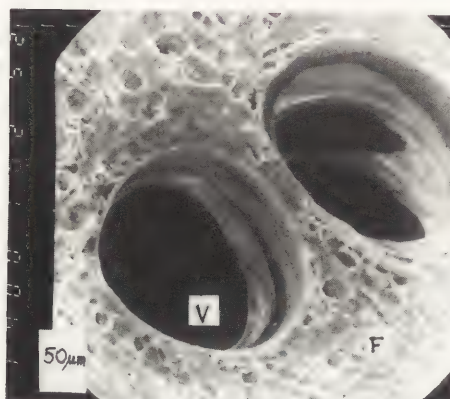


Figure 7.

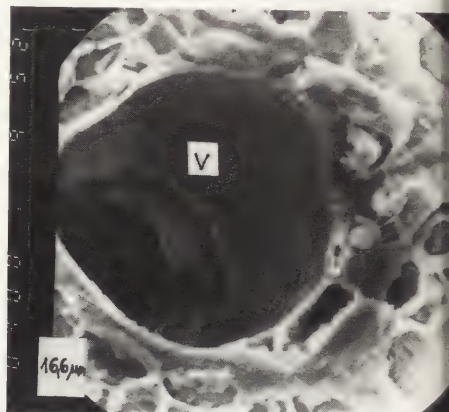


Figure 8.

Figures 7. and 8. Scanning electron micrograph of satisfactorily conserved waterlogged oak, transverse plane. The fiber cells /F/ are mostly filled with sucrose, the vessels /V/ are distinguishable as empty holes. The shapes of the vessels and fiber cells are similar to the undeteriorated oak - there is no sign of collapse. The micrograph was taken from sample C, in Fig.1.



11. Sucrose can be easily extracted from treated wood by water, so conservation can be reversible if necessary.

We consider, that because of these advantageous features, the sucrose conservation method will spread widely and the frequency of usage will match that of PEG. In our opinion thick, large wooden objects can be treated successfully with sucrose. For success with large objects sucrose must bulk cell cavities and diffuse evenly across the total cross-section.

With our method the waterlogged wood can be conserved at room temperature successfully, if the necessary time for diffusion is allowed for.

#### References

1. Powell, W.: Verfahren zum Vulkanisieren und Härten von Holz  
DR. Pat. 163 667 /1903/
2. Powell, W.: US Patent 755.240/1904/
3. Stamm, A.J.: Minimizing wood shrinkage and swelling. Treatment with sucrose and invert sugar.  
Ind. Eng. Chem. 29 /1937/ 7,883-885
4. Gratchew, J.D.; Kovalenkow, A.G.: Holztränkung mit Zuckern zur Erhöhung seiner Wasserfestigkeit.  
Lesochim. Promot. 3/1940/ 9,29-33.
5. Tiemann, H.D.: Wood Technology  
3rd Ed., Pitman, New York /1951/
6. Vinokurov, D.M.: Variation on swelling, hygroscopicity and chemical composition of wood impregnated with glucose during heat and pressure treatment.  
Nanc. Trudy Ljvovskogo Lesot. Inst. 1/1954/ 90-100.
7. Anon: Pickling old boats in alcohol  
New Scientist 63 No 904/July 1974/
8. Art and Archeology Technical Abstracts 12-226; 11-582.
9. Barkman, L.G.; Bengtsson, S.; Hafors, B.; Lundvall, B.; Processing of waterlogged wood, in Proceedings of the Pacific Northwest Wet Site Wood Conservation Conference, Vol. I. Neah Bay WA/1976/
10. Grattan, D.W.; McCawley, J.C.; Cook, C.: The potential of the Canadian winter climate for the freeze-drying of degraded waterlogged wood: Part II.  
Studies in Conservation 25/1980/118-136.
11. McCawley, J.C.: Waterlogged artifacts: the challenge to conservation Canadian Conservation Institute Journal 2 /1977/17-36
12. Grosso, G.H.; Experiments with sugar in conserving waterlogged wood ICOM Committee for Conservation  
6 th Triennial Meeting, Ottawa /1981/ Preprints 81/7/7/1-9/
13. Grattan, D.; Advances in the conservation of waterlogged wood 1981-184. ICOM Committee for Conservation  
7th Triennial Meeting, Copenhagen /1984/Preprints 84.7.8-11.
14. Parrent, J.M.: The conservation of waterlogged wood using sucrose, paper presented to the joint CUA/SHA Meeting Denver, Colorado, January 1983.
15. Parrent, J.M.: The conservation of waterlogged wood using sucrose Master's Thesis, Texas, A and M University, College Station Texas /USA/1983/
16. Parrent, J.M.: The conservation of waterlogged wood using sucrose, Studies in Conservation 30. /1985/ pp.63-72.
17. Lange, N.A.: Handbook of Chemistry, 1106, 1143-1145.  
9th Ed. Handbook Publishers, Inc. Sandusky, Ohio/1956/
18. Murray, H.: "The Use of Mannitol in Freeze-Drying Waterlogged Organic Material, "The Conservator, No. 9 /1985/ pp.33-35.
19. Cook, C., and D.W. Grattan: A Practical comparative Study of treatments for waterlogged wood - Part III - Pretreatment solutions for freeze-drying, in Waterlogged Wood, Study and Conservation, Proceedings of the 2<sup>nd</sup> ICOM Waterlogged Wood Working Group Conference, Grenoble 1984 pp. 219-239.





## SUMMARY

In the Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference (1), Rosemarie Johnson reported on the recovery of Roman and medieval waterfront structures from the site at Billingsgate in the City of London, excavated by the Museum of London between January 1982 and March 1983. This paper covers the subsequent conservation and reconstruction of one of these structures and the use of computerised axial tomography for the non-destructive dendrochronological dating of some of its timbers.

## THE CONSERVATION, RECONSTRUCTION, AND DENDROCHRONOLOGY OF A MEDIEVAL WATERFRONT REVETMENT FROM LONDON

Katharine Starling  
Senior Conservator  
Museum of London  
London Wall, London EC2Y 5HN, UK

Introduction

Four waterfront revetments were recovered from the site, from Roman, Saxon, Norman and 13th century contexts. The 12th century revetment is a particularly fine, front-braced structure (fig 1) and it was decided to attempt to raise money to conserve it before the others in time for an exhibition on the archaeology of London, "Capital Gains", planned for Autumn 1986. The other three revetments, plus this one, are ultimately to go on display in a proposed new museum on London's docklands.

Storage

All the wood is stored until conservation in two large tanks in the museum's carpark. One tank, a wooden structure lined with polythene sheeting, has lasted well but the other, a flimsier construction of Dexion framing and wooden sheets also lined with polythene sheeting, has had to be replaced. For this purpose a collapsible plastic tank held up with scaffolding, of a type used by the Mary Rose Trust and supplied by a marine firm, J. W. Automarine (2), has been used. This has proved to be a successful, economic and easily constructed system. The only modification necessary has been to enclose it with cheap wooden panels in case the bulging yellow plastic sides prove too great a temptation to vandals. Both tanks have floating lids of 'bubblepack' polyethylene to reduce the amount of oxygen available and, over this, black plastic sheeting to reduce exposure to light. This arrangement has kept fungal growth to a minimum.

Dendrochronology

The wooden structures are an important source of dendrochronological dating evidence for the site. The usual way to sample wood for this purpose is to saw across the timbers in order to reveal a good cross-section of the growth rings. This is obviously not suitable for wood destined for display and so other methods of obtaining the necessary information were



Fig. 1: The 13th century revetment on excavation.  
(Photo: Museum of London)



investigated. Attempts to take cores from the wood at right angles to the growth rings using an incremental borer were not successful as the action of the borer tended to compress the wood therefore distorting the results. It also proved difficult to remove the core without breaking off the soft, spongy outer layer which is very important for calculating the felling date. In the end most of the wood was sampled by taking a "V"-shaped wedge from a hidden side of each timber. It was decided, however, that the cladding planks from the 13th century structure should not be sampled in this way as it was necessary to view the structure from both sides as there were important carpenter's marks to be seen. In addition, the planks were too thin to reveal enough growth rings in this way. It was therefore decided to investigate two non-destructive methods of viewing the internal morphology of organic specimens, nuclear magnetic resonance (NMR) and computerised axial tomography (CAT scanning), both of which are used extensively in medicine and have been suggested by several authors as ways to study organic artefacts (3,4,5).

These "body scanners" are used to produce images of "slices" through a patient, which can be taken at any angle; therefore, in theory, they could show growth rings in timbers from the optimum angle for dendrochronology. Both methods are extremely expensive, and it would usually be unjustifiable to hold up an overstretched hospital department in order to process archaeological material. Fortunately a firm that manufactures equipment for both these processes, Picker International, was interested in the problem and suggested trying out the techniques while they were installing and testing plant in a new hospital department. A small trial using NMR scanning proved to be unsuccessful but a good image was obtained using a CAT scanner.

#### CAT Scanning of the Cladding Planks (6)

Following this encouraging trial the cladding planks were all taken to the Mount Vernon Hospital in North West London one evening where staff from Picker International processed the material with representatives from the Museum of London's Conservation and Environmental Departments and from the National Maritime Museum. All the timbers were radiographed on the CAT scanner and the images stored on disc to be processed later. It was possible to see the images on a screen in a separate room during the exposures and therefore change the angle of the beam to the optimum position. Several factors affected the final image (7). Because the resolution was 1mm, only the rings in the faster grown timbers showed up clearly. However, some of the timbers have been dated in this way. Analysis is assisted by the ability of the image analysis program to display densities on a chosen line across the image as a line graph (fig.2).

#### Conservation

Conservation of large waterlogged timbers is always expensive and time-consuming. The two main methods currently most used are bulking with polyethylene glycol (PEG) over a long period and soaking in a more dilute solution of PEG followed by freeze-drying (8). The Museum had to decide which method to use and whether it would be more economic for the work to be carried out on contract. Construction of a freeze-drier of sufficient size was definitely out of the question. It was felt that, as the Museum did not envisage conserving large timbers from many sites, it would not invest in large heated PEG tanks. In view of this and the fact that, if the revetment were to be displayed in "Capital Gains", there was only a limited amount of time available, it was decided to investigate contracting out the freeze-drying of the timbers.

Consortium Conservation (9) was the only firm in the UK to have equipment (impregnation tanks, freezers and a freeze-drier) large enough for the timbers, some of which were up to 2m long, and the expertise to carry out the work. Trial pieces were freeze-dried from 20% PEG 3400 solution. The results were encouraging and in the Autumn of 1985 all the timbers were taken up to Dundee for treatment.

It was decided to use the PEG twinning technique recommended by Per Hoffman (10, 11). The timbers were soaked in 10% v/v PEG 400 for 4 weeks, then transferred to 10% w/v PEG 4000. This solution was increased to 20% over a further 16 weeks. They were then frozen and freeze-dried. Freeze-drying each batch took around 3 weeks, the progress being monitored by weight loss. When the timbers had adjusted to the ambient temperature and humidity, a solution of 80% w/v PEG 3400 was brushed onto the surface of each piece.

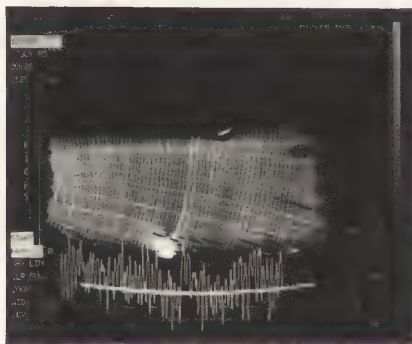


Fig. 2: CAT scan of a timber. The rings date from AD 1105 to AD 1177. The plot at the bottom is the density along the white line.  
(Photo: Picker International)



### Packaging and Results

A specialist packing firm built sturdy wooden crates lined with expanded polystyrene in which to return the timbers to London. Consortium Conservation packed the crates which were unpacked in London by the Museum Conservation Department.

None of the timbers appeared to have been damaged in transit.

The treatment was successful for most of the timbers. The cladding planks, square-cut uprights and base-plate showed little signs of cracking or cross-hatching. However, the front braces, which are little more than roughly dressed branches and were already split on excavation, did show signs of further splitting. This type of wood is always difficult to treat and splitting often occurs.

### Reconstruction

A plinth was constructed to represent the slope of the Thames foreshore. For the temporary exhibition it was decided to only view the revetment from one side. The cladding planks were therefore fixed to a backboard first. For this the original peg holes for the structure were used. Wooden dowels of the same diameter as the peg holes were inserted and screwed into place on the backboard. The planks were hung from these. The main base-plate was then positioned and the uprights inserted. These were in turn fastened to the backboard with long screws inserted in concealed positions. The raking braces and their own base-plates could then be placed in position. Two of the cases the braces had to be reinforced with wooden dowelling and supported with V-section metal strips padded with PLASTAZOTE (12) foam (fig. 3). The plinth and dowels were then painted and the various loose pieces of wood found around the waterfront added to the display.

The revetment has now been on display five months and, apart from a layer of dust, shows no adverse effects. It has formed a splendid introduction to the exhibition and attracted a great amount of interest from visitors.

### Acknowledgements

The work above was carried out by many people. My thanks go to my colleagues in the Conservation Department, especially to Suzanne Keene who initiated most of the work and whose idea it was to try CAT scanning. Also to Ian Tyers of the Environmental Department who interpreted and monitored the dendrochronology experiments and Cliff Thomas of the Technicians Department who carried out most of the reconstruction work. Picker International and the Mount Vernon Hospital were both extremely generous with time, personnel and ideas and Consortium Conservation's enthusiasm helped to get the project under way.



Fig. 3: Supporting the raking braces.  
(Photo: Museum of London)

Several City of London firms and trusts contributed to the substantial cost of conservation and transportation, and their generosity is gratefully acknowledged.

#### Notes

1. Rosemarie Johnson, "Large Waterlogged Timber Structures Excavated on the Billingsgate Excavation, London 1982," Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference, (Grenoble, August 1984), pp 63-69.
2. J. W. Automarine, Hempstead Road, Holt, Norfolk, UK.
3. H. Ellinger, I. L. Morgan, R. Klinksiek and F. Hopkins, "Tomograph Analysis of Structural Materials," Proceedings of Imaging Applications for Automated Industrial Inspection and Assembly, 19-20 (Washington DC Society of Photo Optical Instrumentation Engineers, 1979), pp 179-186.
4. R. E. Tout, W. B. Gilroy and A. J. Clark, "The Use of Computerised X-Ray Tomography for the Non-Destructive Examination of Archaeological Objects," in Archaeophysika 10 (Proceedings of the 18th International Symposium on Archaeometry and Archaeological Prospection, Bonn, March 1978), pp 608-616.
5. A. Habermehl and H. W. Ridder, Method and Apparatus for Testing Materials such as Disease in Living Trees, Canadian Patent No. 1,138,576. issued 28/12/82.
6. Ian Tyers, "Tree-ring Dating by X-Ray Scanner," The London Archaeologist 5, no. 4 (Autumn 1985) pp 87-89.
7. Ibid.
8. Many authors have discussed the conservation of wood using PEG. For recent reports see Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference (Grenoble, August 1984), eds David Gratten et al.
9. Consortium Conservation, Victoria Dock, Dundee, UK (director: Howard Murray).
10. Per Hoffman, "On the Stabilization of Waterlogged Oakwood with PEG. Molecular Size versus Degree of Degradation," Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference (Grenoble, August 1984), pp 95-115. Also papers by other authors in the same volume.
11. Per Hoffman, "On the Stabilization of Waterlogged Oakwood with PEG. II. Designing a Two-Step Treatment for Multi-Quality Timbers," Studies in Conservation 31, no. 3 (1986) pp 103-113.
12. PLASTAZOTE is a low density polyethylene foam supplied by BXL Plastics, Mitcham Road, Croydon, CR9 3AL, UK.



# Working Group 9

Textiles

Textiles





## MEMBERS

Barta\* (Czech.)  
 Ballard\* (U.S.A.)  
 M. Carter\* (Australia)  
 Finch\* (England)  
 Hutchins (U.S.A.)  
 P. Hersh (U.S.A.)  
 Timar\* (Hungary)  
 Schaffer (Canada)  
 Kerr\* (Canada)  
 Weiland\* (GFR)  
 Ordonez (U.S.A.)  
 Masschelein-Kleiner\* (Belgium)  
 Block\* (U.S.A.)  
 Eastop (England)  
 Moller\* (Sweden)  
 Wallenberg (Sweden)  
 Ostergard\* (Denmark)  
 Keyserlingk\* (Canada)  
 Burnham (Canada)  
 Roelofs (The Netherlands)  
 Strate (GFR)  
 de Boeck (Belgium)  
 Schaefer-Masson\* (France)  
 Socorro Mantilla de los Rios\* (Spain)  
 Pertegato\* (Italy)  
 Varoli-Piazza (Italy).

Members whose names are marked with an \* have offered to collect information on current research in their area and send this to the coordinator.

## TRIENNIAL OVERVIEW

Coordinator  
 J.H. Hofenk de Graaff  
 (The Netherlands)  
 Assistant Coordinator  
 M. Flury-Lemberg  
 (Switzerland)

## PROGRAMME 1985-1987

1. Translation and publication of a booklet on "Basic Principles of Textile Conservation" in English, French, German and Spanish.
2. Research on the degradation of silk and conservation of silk textiles; preparation of a bibliography on the weighting of silk.
3. Investigation into the identification and influence of various spots in textiles and the effects of spot removing processes.
4. Experiments on the effect of dry-cleaning solvents on ancient textiles.
5. Further study of degradation phenomena affecting cellulose.
6. Investigation into conservation problems of modern textile art, including degradation caused by fire retardants and modern textile adhesives.
7. Continued research on the tension created in vertically hung textiles by various stitching techniques.
8. Further analysis of natural dyestuffs and their fading properties.
9. Publication of a newsletter based on contacts with regional groups outside of ICOM concerned with the conservation and study of historical and cultural objects.

## SUMMARY

The translation of the booklet on "Basic Principles of Textile Conservation" into English and French will be done by ICCROM. The German version is now being edited and a translation into Spanish has been discussed.

Research on the degradation of silk fabrics of the 18th and 19th century has been done by M.A. Becker, S.P. Hersh, P.A. Tucker and A.W. Waltner from the School of Textiles at North Carolina State University and a first part is presented here.

The influence of Tetrachloroethylene as a cleaning agent on historic textiles with particular attention to future prolonged storage has been studied by T.N. Gromina in Moscow. The effects of a cleaning agent based on water, ethanol and perchloroethylene on fibres and dyes of museum objects are discussed by V.P. Golikov and S.V. Ustinov, Moscow.

A further contribution to the study of degradation phenomena affecting cellulosic textiles is the paper presented by I. Block and A.M. Roy from the University of Maryland. The role of "humid conditions" in the artificial ageing of cellulosic materials has been discussed in a paper by P. Calvini from the Istituto Centrale per la Patologia del Libro.

R. Rothhaar and E. Fischer from the Museum of German History in Berlin/GDR present their approach to the problem of consolidating double sided painted or embroidered flags.

Three papers present further research into the identification of natural dyes mostly in connection with fading properties.

Reference sets in the Determination of Mordants on Archaeological Fibres by Energy Dispersive X-Ray Spectrometry were investigated by C.N. Nelson from the Department of Textile and Clothing, North Dakota State University.

Preliminary results on a research on detergency are presented by N. Eastaugh from the Textile Conservation Centre at Hampton Court Palace.

J.M. Katchanova from the Kremlin Museum in Moscow presents the possible use of non-woven thermoplastic materials for the consolidation of fragile textiles.

The possible use of synthetic polymers as consolidating agents for impregnation of fragile textiles and papers is discussed by a group of authors from the Hermitage Museum in Leningrad.

Two contributions, one by L. Morrison from the Museum of London, the other by E.E. Peacock from the Universitij of Trondheim Museum discuss treatment but above all mounting solutions for archaeological textiles.

G. Matefy from the National Centre of Museums Budapest presents a case study: The restoration of a caucasian carpet from the early 19th century.

Another case study is presented by F. Pertegato from the Centro Restauro Manufatti Tessili in Milan on the conservation of the canvas work upholstery of the 12 Brustolon chairs at the Ca'Rezzonico in Venice.

#### OTHER ACTIVITIES

Incoming reports on current activities have been published in the Committee's Newsletter. The following information has reached the coordinator until February 1987.

##### Canada

A recent development at the Canadian Conservation Institut is the formation of "Research Groups" with the key objective to increase the amount of conservators input into the planning and evaluation of research.

The first goal of the "Paper and Textile Research Group" was to review the needs of the paper and textile conservation fields and to identify and define possible research projects. A final report will be available in Spring 1987.

Also of interest to textile conservators is the CCI's adhesive Testing Programm were 25 polyvinylacetates and 25 acrylic adhesives are being tested.

##### Europe

Germany F.R.: In preparation for 1987 is a publication by the Bayerisches Landesamt für Denkmalpflege in Munich on the Textile finds in a grave of the Bamberg Cathedral as well as the conservation and new presentations of the so-called "Heinrichs gewander" (around 1300) from the Old Chapel in Regensburg.

Hungary: Money has been found to finance the scientific investigation of the world famous, Esterhazy Collection of about 60 textiles of extraordinary value from the 16th -18th century. A new branch for the study of textile conservation will be established at the Budapest Academy of Fine Arts.

The Hungarian National Museum has started on the restoration of "King Mathias' throne tapestry". At the Museum of Applied Arts conservation and restorationwork is carried out on the so-called "Mathias mantle", from the 16th century, "the Niklos Esterhazy dolman" from the 17th century decorated with heavy metal threads and a renaissance horsecloth decorated with precious stones and metals.

Italy: The conservation laboratory for textiles at the Istituto Centrale de Restauro in Rome has started to develop a "checklist" to determine the state of conservation of a textile to facilitate the planning of conservation treatments on a national level.

In March 1987 a Conference is to be organized in Florence on "Tapestries in historic houses, study and methods of conservation". A conservation workshop at the Galleria del Costume at the Pitti Palace in Florence carries out conservationwork on the funerary robes of the Medici family.

The Netherlands: The Textile Commission of Museums has organized one day symposia on the following subjects: Tapestries, Underwear, Indigo, Chintz, Kashmir Shawls. All subjects were treated from a historical, technological and conservation point of view. The proceedings are published.

In collaboration with the Central Research Laboratory in Amsterdam a study week "Introduction to Textile conservation" for curators is organized each year.

New Zealand: Although there are a number of important and varied textile collections in the country, only 1 conservator is working exclusively for textiles and is partly funded to work nationally. The National Museum of New Zealand has a reaearch project with Otago University on the "Causes of deterioration of textiles made from Phormium Tenax (New Zealand Flax, no relation to linen) or "Harakeke" (as it is called in Maori).

United States: The following research reports at professional meetings sound particularly interesting:



At the Harpers Ferry Regional Textile Group Eighth Textile Preservation Symposium held November 6-7, 1986 at the National Museum of American History, Washington, D.C.:

"The problem of Formaldehyde in Museum Collections," Fane Carpenter, Assistant Objects Conservator, The Brooklyn Museum, Brooklyn, NY and Pamela Hatchfield, Assistant Conservator, Research Laboratory, Museum of Fine Arts, Boston, MA.

"Plywood as a Storage and Display Case Material," Ann Brooke Craddock, Supervisory Paper Conservator, National Museum of American History, Smithsonian Institutions, Washington D.C.

"Developing Conservation Techniques for Torah Ark Curtains," Patsy Orlofsky, Executive Director, The Textile Conservation Workshop, South Salem, NY.

At the Association of College Professors of Textiles and Clothing Ninth National Meeting held October 22-25, 1986 at The Westin Galleria Hotel in Houston, Texas:

"The Effectiveness of Ultraviolet Filtering Sleeves in Reducing Fading of Natural Dyes," Dr. Patricia Crews, University of Nebraska, Lincoln, Nebraska.

"An Evaluation of Antioxidants for the Conservation of Museum Textiles," Kimberly Asche and Dr. Patricia Crews, University of Nebraska, Lincoln, Nebraska.

Health related information important to textile conservators as well as any consumer who uses paradichlorobenzene:

Dr. Regina Santella, researcher at the Columbia University School of Public Health, New York, NY, reports that paradichlorobenzene has been shown to be an animal carcinogen. The test involved force-feeding high doses of the chemical to rodents, but in the United States extrapolation of animal test results to indicate the potential health effects in humans is well accepted in the scientific community although the procedure still is controversial. These are results that we cannot afford to ignore.

At the University of California Prof. Zeronian is preparing an atlas of insect induced damage to natural fibres.

At the University of Delaware F. Mayhew investigates the usefulness of sodium borohydrate treatment on dyed textiles.

The effect of pesticides on the color and properties of textiles are being investigated by M. Ballard at the Smithsonian Institution.

The effects of dry cleaning on fabrics by M. Wentz at the University of North Carolina and Jane Carpenter at the Brooklyn Museum investigates formaldehyde emissions from storage cases.

All the activities mentioned here are just a selection of those carried out all over the world but they represent the basic aims of the working group "Promotion of exchange of experience in the field of conservation of textiles and the interdisciplinary cooperation between conservators, curators and scientists.





## Summary

Crosslinked synthetic latex has been identified as one of the adhesives used in adventitious repair to oriental carpets and other textiles. A method to remove this latex was developed. The experimental treatment method uses an aqueous solution of ammonium acetate, then air drying, followed by drycleaning with 1,1,1 trichloroethane.

THE REMOVAL OF CROSSLINKED SYNTHETIC LATEX FROM CARPETS:  
PRELIMINARY RESULTS

Mary W. Ballard  
Senior Textile Conservator  
Conservation Analytical Laboratory  
Smithsonian Institution  
Washington, D.C. 20560 USA

History.

Several decades ago, collectors, dealers, artists, and oriental rug restorers--without any review of product literature, scientific study, or accelerated ageing data--casually treated their oriental rugs and fiber art with water emulsible adhesives ("latex"). Today these oriental rugs, hooked rugs, and needlepoint carpets, as well as modern fiber artworks, are beginning to appear in textile conservation laboratories with post-production latex backings on the verso of the object.

The latex backing was used to secure repairs to the pile of the rug, to hold new repair knots in place, and to prevent carpets from sliding on floors. Nineteenth century hooked rugs and needlepoint rugs can also be found which have foundation fabrics (substrates) smeared with latex to hold tufts of yarn or rag pile in place. The fiber artist Sheila Hicks has used a layer of latex to "hold in the canvas the bits of wool that were not knotted" [15]. In this instance, the latex "saved time" as well.

A latex--a polymeric emulsion adhesive--provided a quick and simple method to repair tears or splits; it temporarily stabilized the weave/pile matrix; and it reduced the slipperiness of the carpet on a hardwood floor. When the latex application was confined to the outside perimeter of the carpet, it could be assumed that the aim or goal of the application was to prevent slippage on a hardwood floor. Wool felt underlayments do not prevent small carpets from sliding; the frictional adhesion between the felt and the floor is not nearly as great as that between the carpet and the felt.

At least one carpet dealer/restorer is known to have treated every small carpet entering his establishment with a latex adhesive backing so that the small area rugs could not slip on the waxed wood floors of his customers [7]. This basis for treatment would not be necessary today as other types of underlayment are available for small carpets. It is likely that this treatment occurred ten or twenty years ago. In almost all the cases, the treatments occurred at least ten years ago; the actual products used were not recorded; and the presence of the polymeric compound has been found to accelerate the deterioration of the rug.

For the textile conservator, the use of a latex backing introduces a material unsympathetic to the natural flexibility of a fabric or carpet. The increased stiffness in the previous portion of the carpet will actually induce damage to the object: the carpet foundation begins to crack. Fracture can also occur in storage from the stress on the foundation while it is rolled, even if the storage tube is of generous diameter. Furthermore, the absorption of the polymeric emulsion into the foundation structure prevents additional repairs at a later time: the foundation weave becomes too rigid to support the manipulation that conventional repair with a needle and thread would require. The fracture itself begins on the verso at the substrate, so that damage is not apparent until the carpet has been examined or until the carpet has already developed major splits.

Examination and Analysis.

Visual Examination. Four carpets belonging to American historical societies and museums had similar patterns of deterioration: a Sultanabade carpet (1850-1875); a Karabagh carpet (mid 19th century), an Iranian carpet (ca. 1875-1900); and a "Brussels" (machine woven) carpet (ca. 1985). On all four, an adhesive backing had been applied only to the back or verso of the object. All four showed increased stiffness in areas of treatment with the polymeric emulsion. Where the latex backing was evident, the carpets had greater damage than where no backing had been applied. The fractures to the weave structure varied from horizontal splits across the warp to wholesale breakage to vertical splits parallel to the warp.



The adhesive backings varied from opaque to translucent; they generally added a yellow appearance to the surfaces of the weave structures to which they had been applied. Each adhesive backing formed a cohesive mass sitting in large measure above the yarn but filling the interstices of the weave structure, as well as those spaces between the fibers on the outside surface of each yarn. The thickness of the polymeric film varied from carpet to carpet and among areas of a given carpet. It may have been applied by brushes or, as reported to the textile conservator examining the Brussels carpet, with painting rollers [7]. Because of the liquid nature of polymeric emulsions, the verso surface of the latex carpet was usually fairly uniform: the polymer flowed before drying.

Most of the latex backings retained some flexibility and tenacity to the fibers and mechanical removal would have only damaged the foundation structure of the carpet. A scalpel could not have safely separated the foundation of the rug from the latex. One carpet fragment did have a more brittle latex: here the polymer could be scratched from the verso with an ivory bone folder, without disturbing the weave structure beneath the polymeric material.

**Solubility Parameter.** A thermoplastic polymeric material can be characterized by the solvents which dissolve or swell it. For each solvent or resin, there are intermolecular forces (dispersive, dipole-dipole, and hydrogen bonding), and each of these factors can be given a numerical value [8, 26]. In order to establish this "solubility parameter" for various latex backings, different solvents were tested on a latex carpet (Iranian) carpet fragment: acetone (47/32/21), ethanol (36/18/46), xylene (83/5/12), toluene (80/7/13), and methyl ethyl ketone (53/26/21). The last, methyl ethyl ketone, performed the best. The polymeric material was softened and slowly dissolved. However, the experimental submersion of two fragments of the Iranian carpet in MEK for 15 hours yielded carpet fragments that retained enough polymeric material to remain stiff, despite the high liquor ratio involved. The spent liquor was decanted and allowed to evaporate and the residue was retained for future tests.

Tests were also conducted on the two types of latex adhesive found on the verso of the "Brussels" carpet. The latices will be termed Adhesive #1 for the older latex and Adhesive #2 for the second and complete backing. Since the backing on the first fragment had responded best to the higher dispersion forces, fairly high dipolar contributions, and lower hydrogen bonding found in the solubility parameter of methyl ethyl ketone, this and similar solvents were used on Adhesive #1. Acetone (47/32/31), cyclohexanone (55/28/17), cyclopentanone (-), diethyl ketone (-), methyl ethyl ketone (53/26/21), methyl propyl ketone (-), and methyl cyclohexanone (-). These ketones loosened the latex enough to soil swabs and blotters with residue. In addition, xylene (83/5/12) and toluene (80/7/13) were tested. While some residue was removed, these solvents were less effective [7].

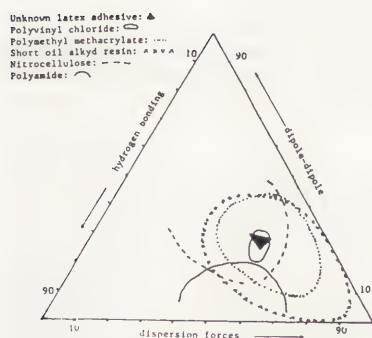


Figure 1. Solubility Parameters.

The process of testing was repeated for Adhesive #2. The results were equivalent to those of the first fragment but a comparison to solubility parameters of known resins suggest what the latex backing is not, more than what it is (see Figure 1). The latex backings examined are not polyamide ("soluble nylon") once used in textile conservation; they are probably not related to any nitrocellulose coating; it is unlikely they are a pure poly(vinyl chloride). They fall outside the range of "short oil" alkyl resin. They do fit the range of solubility of poly(methyl methacrylates) [26].

Conventional conservation cleaning methods that depend on dissolving the material to be removed are not suitable for the removal of latex backings. Initial work on the solubility parameter of two extant latex repairs made this limitation quite apparent. Whether or not the polymeric material was crosslinked or oxidized, solvent systems that began to remove any fraction of the polymer did so with bad results. The polymeric material that was removed was readily absorbed into the fiber substrate of the adjacent warp and weft. The stiff object actually becomes more rigid with the removal of the latex from the verso surface. Solvents applied to non-porous surfaces can remain on the outside of the object but wool, cotton, or jute--even if the fibers are spun and plied--retain an absorbency that prevents simple removal with solvents by swabs or blotters. Thus, the conventional methods used to remove aged painting varnishes cannot be transferred to this particular polymeric removal problem.



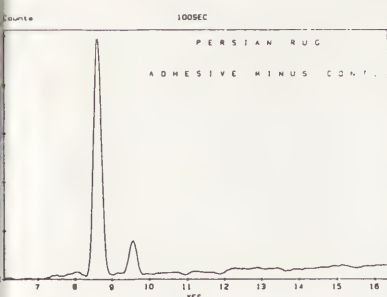


Figure 2. X-ray fluorescent spectrum of unknown adhesive removed from Persian carpet.

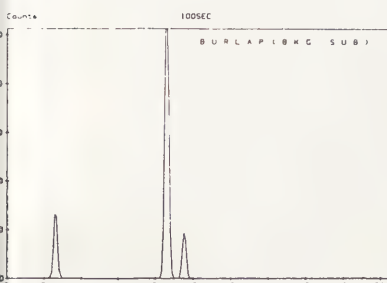


Figure 3. X-ray fluorescent spectrum of unknown adhesive removed from tertiary backing (repair) of "Brussels" carpet.

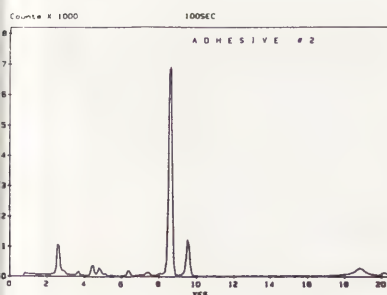


Figure 4. X-ray fluorescent spectrum of Adhesive #2.

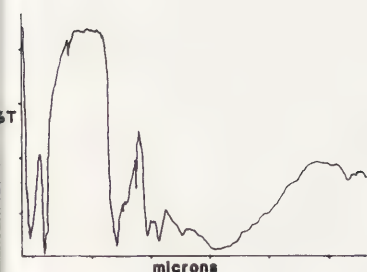


Figure 5. Infrared spectrum of unknown adhesive residue from Iranian carpet.

**X-Ray Fluorescence.** While some polymers will crosslink without inorganic agents, the detection of typical inorganic additives for latex could indicate the presence of an inorganic crosslinking agent, and suggest the type of polymer in question. If the latex adhesive were a "true" latex, of natural rubber, few inorganic ions would be present. If the latex were entirely synthetic, the inorganic materials found might indicate which polymer is present.

Three sets of polymeric samples were taken to the Analytical Laboratory in the Conservation Department of the National Gallery. There, a Kevex energy dispersive X-Ray Fluorescence unit is set up with barium and rhodium targets; the collimator source is 6mm; the detectors vary from 2 to 6 mm. In all tests, an accumulation time of 100 seconds was deemed sufficient.

One carpet fragment was analysed both in an undisturbed area and in a latex coated area. When the two results were compared, and the inorganic background of the carpet subtracted from the residue/carpet fluorescence, the result showed no trace of inorganic elements on the specimen, a result which indicates that the polymer has an entirely organic chemical composition. Next, the latex adhesive residue from the methyl ethyl ketone immersion test of the Iranian carpet fragment was tested. The spent liquor had been allowed to dry and had been held on an aluminum foil surface. Again, the foil was analysed and subtracted from the final result. The residue showed a substantial amount of zinc (Figure 2). Although the results of X-ray fluorescence on thin polymeric films cannot be calculated in a quantitative manner, the strength of the peaks do suggest the presence of enough zinc to accelerate the polymerization of isoprene or to crosslink a poly(acrylic acid) [1].

A piece of burlap which had been used as a tertiary backing on the Brussels carpet was assayed. After subtraction for the impurities within the burlap itself, the adhesive residue on its edge also revealed a large amount of zinc, together with an indeterminate amount of chlorine (Figure 3). In fact, the quantity of zinc required resetting the instrument to incorporate the top of the peak. The chlorine is "attenuated" (reduced in intensity) because its X-rays are absorbed by the air, and the amount of chlorine cannot be determined [1]. The presence of the chlorine could indicate a polyvinyl chloride copolymer in the latex.

X-ray fluorescence analysis was also carried out on a small fragment from the Brussels carpet. Once again, significant amounts of zinc and chlorine were detected. In this instance, small amounts of calcium and iron are present also. Finally, a small sample of burlap impregnated with Adhesive #2 was tested. This sample could not be run against a control, since no area of the burlap was unaffected by the latex adhesive. Nevertheless, only zinc and chlorine were present, with a small amount of iron (Figure 4). Thus, the results of the analysis of the Iranian carpet, the adhesive on the tertiary backing of the Brussels carpet, its Adhesive #1 and its Adhesive #2 all appear to have some of the same inorganic components.

**Wet Chemical Testing.** Sulfur's position is detectable by XRF, but its absence was specifically confirmed by wet chemical testing. A reducing solution was made containing 10 gr of stannous chloride and 10 ml of concentrated hydrochloric acid and added to 55 ml of deionized water. Lead acetate paper was prepared using a supersaturated solution of lead acetate in deionized water. Samples were taken of the adhesive/burlap tertiary backing, a burlap backing blank (no adhesive), the Adhesive #1 on a thread, a blank control thread, and the impregnated Adhesive #2/burlap. Each sample was individually placed in a small petri dish and slowly heated. Each petri dish was covered with a lead acetate paper. No brownish black stain on the paper occurred to indicate sulfur [13].

**Infrared Spectroscopy** is a standard method of resin analysis. There are, however, problems associated with interpreting the spectra of samples of degraded polymeric mixtures, and with distortion of spectra due to additives. Nevertheless, it was hoped that a comparison with the spectra of known polymers would eliminate some compounds from consideration.

A Mattson Alpha Centauri Fourier transform infrared spectrophotometer was employed. Some of the samples were prepared by simple grinding to a powder that was then spread out on a



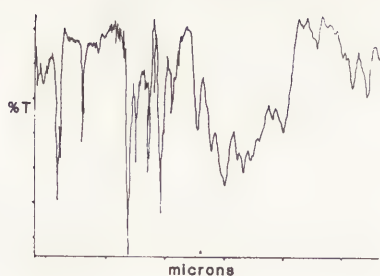


Figure 6. Infrared spectrum of Adhesive #2 from "Brussels" carpet.

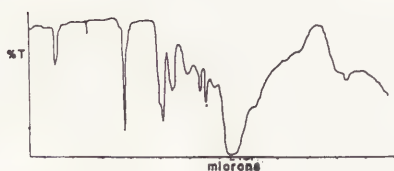


Figure 7. Infrared spectrum of the tetrapolymer vinylidene chloride/acrylonitrile/methyl acrylate/itaconic acid (91:4.5:4:0.5).

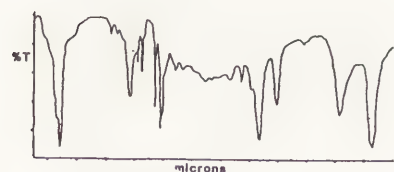


Figure 8. Infrared spectrum of the terpolymer of butadiene/styrene/carboxylic acid (50:45:5)

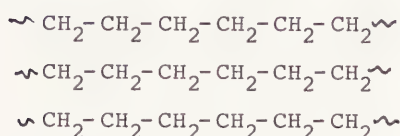


Figure 9. The structure of poly(ethylene), a linear polymer.

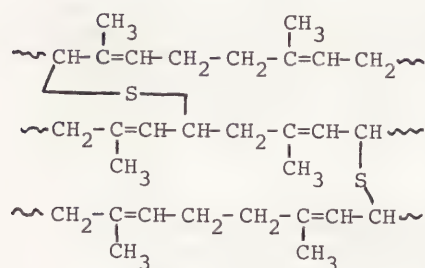


Figure 10. The structure of vulcanized rubber (poly (cis-1,4-isoprene), a crosslinked polymer.

potassium bromide film; others were dispersed in potassium bromide pellets. Adhesive #2 required dispersion with methylene chloride. A control sample of pure potassium bromide was made as well. The spectra of Adhesives #1 and #2 are closer in appearance to each other than to that of the MEK/latex residue, although the spectra do share some common characteristics (see Figures 5 and 6). All of the samples show some absorbance at 1647-1653 wavelenghts; at 1457 or 1458; and at 1375-1386. The common reading at 2360 is that of carbon dioxide. While the Iranian carpet polymer and Adhesive #1 share a possible carboxyl salt peak at 1540, the Iranian carpet polymer and Adhesive #2 share a possible aromatic alcohol moiety with similar peaks at both 3425-3428 and 1239-1243. The two adhesives share three peaks at 1111, 1033, and 908-910, which suggest aliphatic ethers, primary alcohol groups, or ionic carbonates [17, 19].

Parallels can be drawn between the spectrum of the vinylidene chloride/acrylonitrile/methyl acrylate/itaconic acid tetrapolymer (91:4.5:4:0.5, Figure 7) and those of Adhesives #1 and #2 more easily than to the spectra of Neoprene, cis-1,4-polyisoprene, styrene/butadiene (62:38) or a terpolymer of butadiene/styrene/carboxylic acid (50:45:5, Figure 8) [20, 21, 24].

### Theory.

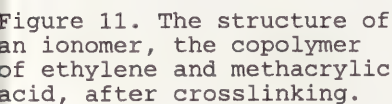
Polymers are divided into two fundamental groups, linear and non-linear, i.e. crosslinked, polymers (see Figures 9 and 10). The emphasis in conservation materials research has been to develop the use of linear, thermoplastic, soluble polymers and to proscribe the use of crosslinking, thermosetting materials for all but special cases [8]. Polymers of both types can be produced by several methods: bulk polymerization (with only reagents and products), solution polymerization, suspension polymerization, and emulsion polymerization. Latex traditionally described the emulsion product of natural rubber, poly(cis-isoprene) dispersed in an aqueous medium. The final, dried product was crosslinked into a three-dimensional network, sometimes by means of sulfur (see Figure 10). Today latex is a generic term for the milky result of an emulsion polymerization where 40-80% solids (polymer) are dispersed, rather than dissolved, in a liquid (usually water) [3, 4, 25].

Tufted carpet technology uses such lattices as adhesives to secure unknotted pile yarns to a primary, woven substrate. Styrene-butadiene rubber copolymers called "SBR's" have replaced natural rubber as the latex adhesive selected. Although butadiene can be crosslinked across its remaining unsaturated bond, a simple, self-curing system has been developed by adding a third carboxylated component polymer. It is this XSBR that is important to the study. If the carboxylic acid groups on each chain react with a divalent metal salt, bridges between XSBR polymer chains are formed. The result is a crosslinked, stable, solvent resistant polymer. Technically, these lattices are ionomers; that is, they are polymers with ionic salt bridges which can be reversibly crosslinked (see Figure 11) [9, 10, 12, 22].

The analysis of the polymeric material suggested a new treatment to remove the latex backing. Solubility parameter testing indicated that the material could be partially, but not entirely, dissolved. X-ray fluorescence showed that the divalent metal crosslinking agent, zinc, was present. Infrared spectra demonstrated that natural rubber latex (polyisoprene) was not present and sulfur was not found during the wet chemical testing.

Instead of wholesale dissolution by a single solvent or group of solvents, a sequential process seemed appropriate. First, the crosslink in the polymer is broken, the crosslinking agent is flushed out, and the uncrosslinked polymeric residue is rinsed out and dried. A second solvent system is then introduced to separate the remaining polymeric material from the object. This second solvent is not chosen on the basis of being a "good" solvent, because the goal is not to dissolve the polymer but only to loosen it from the object. A "good" solvent would dissolve the polymer and allow it to migrate into the fibers of the textile. Therefore a "poor" solvent is used, one that would be on the edge of the solubility parameter so that absorption into the fibers could not take place [27]. At this point, the polymeric material could be treated like any other foreign solid soil particle and abstracted by a combination of gentle agitation and flushing.





However, wool substrates would be adversely affected by ammonia. Alkali can seriously degrade any protein; it can hydrolyse peptide bonds and amide side-chains. Wool is particularly susceptible to alkali damage since the disulfide bonds which provide the cystine crosslink can be destabilized by alkali [16]. An alternative ammoniacal agent, often used with wool dyeing, is the ammonium salt of acetic acid, ammonium acetate. This is actually neutral at room temperature (3.5 g/l has a pH of 6.96). When used in dyeing neutral metal complex dyes, the addition of ammonium acetate (3% based on the weight of the sample) insures a slightly acid bath as the ammonia evaporates (the same solution will have a pH of 6.38 at 80°C.[5, 16].

Four samples, each approximately one inch by three quarters of an inch, were cut from a loose portion of the tertiary backing of the Brussels carpet (see Figure 12). Each sample had about the same amount of latex backing upon the verso. Each sample weighed between 0.14 and 0.16 gr. Solutions of 10% ammonium acetate in deionized water and of 10% ammonium hydroxide in deionized water were made up. The samples were treated at room temperature (70°F + 2°F) to the following solutions:

- Sample 1) 5 ml 10% ammonium acetate (circa 3.2% o.w.s.)  
 Sample 2) 5 ml 10% ammonium hydroxide (circa 3.2% o.w.s.)  
 Sample 3) 2.5 ml ethanol + 2.5 ml 10% ammonium hydroxide  
 (circa 1.6% each component o.w.s.)  
 Sample 4) 2.5 ml ethanol + 2.5 ml 10% ammonium acetate  
 (circa 1.6% each component o.w.s.).

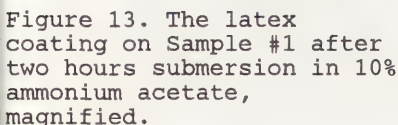
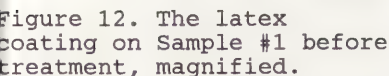
The samples were observed under low powered magnification at various intervals (see Figure 13). After fifteen minutes of submersion, the latex backing had become opaque and the color of milk. Its distribution and density was strikingly visible. The samples all showed greater flexibility--a softer handle--than that exhibited prior to submersion. In addition, all four samples had small areas of their latex surface dotted with orange spots; the density of this unexplained orange coloring increased at the highest points of the yarn; its occurrence was not related to the density of the original latex film. After one hour, Samples 2 and 3 exhibited indications of separation of the polymeric layer: the latex was beginning to break up into parts, although these parts seemed to remain attached to the fabric substrate.

On the recto, it was apparent that the latex had also swollen. The interstices of all four samples were filled with the same soft opaque polymer. Although the difference between fifteen minutes and two hours did not seem pronounced for the recto of Sample 3, for the recto of Sample 4, the change over just one hour was clear. The samples were allowed to sit immersed in their respective solutions for a total of four hours. At the end of that time, the pH of all four sample solutions was taken, using Special Indicator Sticks made by E. Merck (Darmstadt, West Germany). The readings were as follows:

- Sample 1) pH 7.0 - 7.5.  
Sample 2) pH 10.5.  
Sample 3) pH 10.0  
Sample 4) pH 6.5 - 7.5.

It should be noted that the solutions at this time had a yellowish caste. Sample 2, which contained 10% ammonium hydroxide, had the strongest coloring, and Sample 4, with half ethanol and half 10% ammonium acetate, had the least coloring. Next, all were individually rinsed in deionized water. The samples themselves were separately set onto clean mylar film and cut in half: one half was air dried, one half dried with acetone.

Sample 1 was selected for the second section of the treatment, based on its final pH, its appearance, and the appearance of its solution. Because infrared spectra of the latices associated with the Brussels carpet had conformed in some respects to the tetrapolymer containing poly(vinylidene chloride), a solvent for that polymer was considered: 1,1,1, trichloroethane. This solvent is also a common dryside spotting agent and easily available. It is not a "good" solvent in the sense that it had lower dispersive





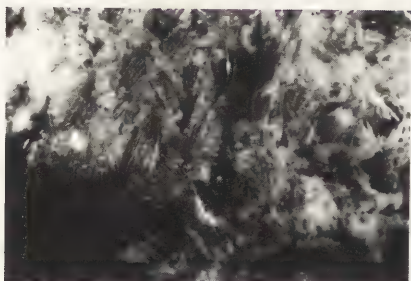


Figure 14. The latex coating on Sample #1 during its first rinse with 1,1,1-trichloroethane, magnified.



Figure 15. The burlap backing of Sample #1 after the final rinse, with no trace of latex on the fibers, magnified.

forces, higher dipolar forces, and lower hydrogen bonding (70/19/11) than the ketones used previously. It did allow the polymeric material to flake off the fabric substrate. Again submersion rendered the latex white and opaque. Under low magnification, the action resembled skin flaking off a sunburned body, but less adhesion was involved (see Figure 14). In fact, the issue of removal was reduced to the problem of flushing away enough of the polymer so that loose flakes were not caught in the loose fibers of the yarns.

Two rinses were able to render Sample 1 visibly free, when dry, of any polymeric material and as flexible to the touch as a fabric which had never been treated with latex adhesive (see Figure 15). At 25X magnification, however, some residue of the latex could be seen in the interstices of the weave. A third rinse rendered the sample virtually clean.

#### Discussion.

Visual examination was sufficient only to show the existence of a problem, not to explain it nor to suggest a remedy. The analytical methods for identification also had benefits and drawbacks. Solubility parameter tests produced the results that led to the other analytical work, although solvent testing itself did little more than show that solvent treatment alone would not work. X-Ray Fluorescence allowed a definitive identification of certain elements in the polymer but did not explain the quantity of inorganics nor the role those inorganic elements played in the adhesive. Yet, XRF analysis did assist the subsequent interpretation of infrared spectra. The infrared spectra of twenty year old mixed polymer adhesives were not easily interpreted. Alterations in the proportions of polymeric constituents change the spectra and the presence of inorganic substituents further complicate the spectra of the polymer. Knowing which inorganic elements were present helped in the interpretation [20, 21].

The precise nature of the polymeric material remains a mystery. It may be that more sophisticated extraction methods, including separation by size exclusion chromatography prior to infrared spectroscopy might allow distinct components to appear. Yet these methods are not readily available to practicing conservators. Inorganic analysis is easier to obtain. Confirmation by wet chemical testing may be available as well. While the exact nature of the polymer is still unclear, the number of possibilities was reduced to reasonable limits with the analytical methods described. This was enough to develop the course of treatment.

#### Conclusion.

The treatment described above provides a useful method for reversing damage previously found irreversible. Antique textiles with partially or fully carboxylated latex backings would, of course, require careful examination to determine whether or not the colorants, the weave structure, the yarn conformation, and the overall condition could withstand the initial swelling of fiber and latex. Carpet and textile conservators make decisions of this type on a daily basis and the protocols are well established. No treatment is suitable for all objects, even those of the same type, history or coloring.

#### Acknowledgements.

The author would like to thank Paul Czubay for providing samples and solubility data. Dr. Charles Tomasino, professor of textile chemistry at North Carolina State University at Raleigh, is thanked for his insight and advice. Walter Hopwood, chemist at CAL, ran the Fourier transform infrared spectrophotometer.



## References

- [1] Angiolillo, P. Consultation with. National Gallery of Art. April 22, 1986.
- [2] Anonymous, "Carpet Latex Suppliers," American Dyestuff Reporter, (June, 1980):36-37.
- [3] Bauer, H.B. and Prah, K. "Untersuchung spezieller Alterungserscheinungen an textschaumen," Meilland Textileberichte, vol. 63 (December, 1982):850-853 ["Investigation of Special Ageing Tendencies of Latex Foams," Meilland Textilberichte (English edition, December, 1982): 837-841].
- [4]-----". "Untersuchung spezieller Alterungserscheinungen an textschaumen," Meilland Textilberichte, vol. 64 (January, 1983): 30-34 ["Investigation of Special Ageing Tendencies of Latex Foams," Meilland Textilberichte (English edition, January, 1983):29-33].
- [5] Bird, C.L. The Theory and Practice of Wool Dyeing, 4th edition. Bradford, Yorkshire: Society of Dyers and Colourists, 1972.
- [6] Braun, D. Simple Methods for Identification of Plastics, translated by E. Immergut. New York: Macmillan Publishing Co., Inc. 1982.
- [7] Czubay, P. Private Communications, 1984-1986.
- [8] Feller, R.L., N.Stolow, and E. Jones. On Picture Varnishes and Their Solvents, revised and enlarged edition. Washington, D.C.: National Gallery of Art, 1985.
- [9] Gilbert, R. D. "The Theory and Practice of Carpet Latex Systems, Proceedings of the Second Symposium on Solving Tufted Textile Problems: A Practical Approach, December 8-9, 1981, edited by R. P. Walker and D.M. Hall. Auburn, Alabama: Department of Textile Engineering, Auburn University, pp. 150-162.
- [10] Grint, M. "Materials and Methods of Back Coating Carpets," Carpet Substrates, edited by P. Ellis. Manchester, England: n.d. pp. 71-79.
- [11] Haslam, J., H.A.Willis, and D.C.M. Squirrell. Identification and Analysis of Plastics, 2nd edition. New York: John Wiley and Sons, 1981.
- [12] John, C.A. "International Developments in Carpet Backing Systems," Proceedings of the 10th Annual Conference: Carpets and Associated Technologies, edited by L.F. Story. Auckland, New Zealand: The Textile Institute, New Zealand Section, 1982, pp. 39-52.
- [13] Koch, P. Microscopic and Chemical Testing of Textiles, translated by C.J.W.Hooper. New York: Textile Book Service, 1963.
- [14] Krause, A., A. lange, and M.Ezrin. Plastics Analysis Guide: Chemical and Instrumental Methods. New York: Hanser Publishers, 1983.
- [15] Levi-Strauss, M. Sheila Hicks. London: Studio Vista, n.d.
- [16] Maclaren, J.A. and B. Milligan. Wool Science: The Chemical Reactivity of the Wool Fibre. Division of Protein Chemistry, CSIRO, Australia: Science Press, 1981.
- [17] The Merck Index: An Encyclopedia of Chemicals and Drugs, 9th edition, edited by M. Windholz et al. Rahway, New Jersey: Merck and Co., Inc. 1976.
- [18] Nakanishi, K. InfraRed Absorption Spectroscopy. San Francisco: Holden Day, Inc. 1962.
- [19] Peters, R.H. Textile Chemistry. Vol. II: Impurities in Fibres; Purification of Fibres. New York: Elsevier Publishing Co., 1967.

- [20] Potting, B and H.Klingenberger. "Alterungsverhalten von SBR-Schaumbeschichtungen," Meilland Textilberichte, vol. 66 (January, 1985):80-82 ("Ageing of SBR-Foams, Meilland Textileberichte (English edition, January, 1985): 104-108).
- [21]-----". "Alterungsverhalten von SBR-Schaumbeschichtungen," Meilland Textilberichte, vol. 66 (February, 1985):143-147 ("Ageing of SBR-Foams, Meilland Textilberichte (English edition, February, 1985): 178-183.
- [22] Saunders, K.J. Organic Polymer Chemistry. London: Chapman and Hall, 1973.
- [23] Schnabel, W. Polymer Degradation: Principles and Practical Applications. New York: Macmillan Publishing Co., Inc. for Hanser International, 1984.
- [24] Silverstein, R.M. and G.C.Bassler. Spectrometric Identification of Organic Compounds. New York: John Wiley and Sons, Inc. 1963.
- [25] Smigielski, E. " The Backcoating Technology of Carpets, Parts 1 to 8," Carpet Technical Information Letter #84 (July, 1985) Ikley, Yorkshire: International Wool Secretariat: 1-80.
- [26] Teas, Jean P. Predicting Resin Solubilities, Technical Bulletin Number 1206. Columbus, Ohio: Industrial Chemicals and Solvents Division, Ashland Chemical Company, 1971.
- [27] Tomasino, C. Course TC591: Chemistry and Technology of Non-Fibrous Polymers. School of Textiles, North Carolina State University at Raleigh, January-May, 1985 (TOTE).



## SUMMARY

A set of fabrics dating from the late 18th to early 20th centuries was evaluated for the presence of inorganic weighting agents by energy dispersive X-ray fluorescence (XRF).

Five of the 13 silk fabric and garment samples were weighted with tin. All of these five were garments from the 1880-1910 period. The black components in these garments all contained iron and tin and also were found to be dyed with logwood. One component also contained copper in addition. Only one garment from this period did not contain tin. The four fabric samples from this period not constructed into garments did not contain tin weighting agents or any other metals. One of these fabrics had black sections which were not dyed with logwood. Two fabrics from the late 18th century and three flag fragments from 1862 showed no evidence of tin weighting.

THE INFLUENCE OF TIN WEIGHTING AGENTS ON SILK DEGRADATION  
Part I. Inorganic Weighting and Mordanting Agents in Some  
Historic Silk Fabrics of the 18th and 19th Centuries

M. A. Becker, S. P. Hersh and P. A. Tucker  
School of Textiles, and  
A. W. Waltner, Physics Department  
North Carolina State University  
Raleigh, NC 27695-8301 U.S.A.

### Introduction

A major variable which contributes to the fragility of silk is the practice of "weighting" that has been conducted for at least 300 years [1,2]. Weighting is the application of generally 30% to 300% of inorganic salts of aluminum, iron, lead, magnesium, tungsten, zinc or especially tin to silk fabrics to increase the body, "hand," "scroop," drape, weight per unit area, etc. It is believed the practice probably originated to recoup the approximately 25% weight loss which occurs when silk is degummed. Later it may have become a fraudulent means of increasing the value of the product which is sold by weight. By the late 1800's, weighting had become an accepted method of preparing silk before its final use.

The light stability of unweighted silk is greatest at about pH 10, but decreases rapidly as the fabric pH becomes higher or lower [3]. Since most weighting compounds are highly acidic, one might expect that weighted silks would be even less stable than unweighted silks. This sensitizing effect of weighting has indeed been shown to occur and is far more detrimental to silks exposed to light than to fabrics stored in the dark [4,5]. However, damage even during storage in the dark is severe.

Several mechanisms have been proposed to explain the degradation of silk in which the presence of metal complexes accelerates the degradation [6]. Because of the fabric sensitivity to weighting, it is apparent that efforts to develop and recommend conservation treatments of silk ultimately will require a knowledge of the nature and amount of weighting materials present in the fabric.

The most common procedure for weighting silk fabrics with tin is to make successive applications of solutions containing stannic chloride and sodium phosphate until the desired level of weighting is achieved. This treatment is followed by immersion in a silicate bath. Weighting is usually carried out prior to dyeing which generally removes a small amount of the weighting agent. In addition to the metals listed above, barium, antimony, cadmium, zirconium, boron, titanium, thorium, chromium, and molybdenum have also been mentioned in the literature as weighting agents [7].

For black fabrics, the situation becomes more complicated since iron was used both as a mordant and a weighting agent in many early methods for dyeing silk black [7,8]. A mordant is a substance applied for the purpose of fixing the color and must be capable of chemically reacting with the coloring agents. Tannins were also known to be employed as organic weighting agents and worked best when fixed with iron. Logwood is a natural dyestuff frequently used in the past to dye silk black. Since it was commonly applied with tannin and iron compounds, it is virtually impossible to distinguish between those compounds used as weighting agents and those used in the dyeing process. Copper compounds have also been used as mordants for logwood dyeing. Since the tannin-iron treatment colors the fabric, it is generally used only when dyeing dark colors.

### Test Samples

Fabrics and garments available for analysis consisted of eleven samples plus three flag fragments from the study collection of the Division of Textiles, National Museum of American History and one sample from the Atlanta Historical Society. Many of the garments are composites consisting of several layers and decorative elements. The fabrics examined were identified as follows:

- 1) Late 19th or early 20th century wedding dress, beige.
- 2) Early 20th century, green fabric with green satin stripes.
- 3) Late 19th or early 20th century white fabric with piping.

- 4) 18th century brocade fabric, green background with a flower and building pattern.
- 5) Late 18th or early 19th century, pink fabric with embroidered metallic flowers.
- 6) Late 19th century vest, 3 layers, black top and lining, gold inner layer.
- 7) ~1901 Edwardian collar piece, green fabric with beige lace and black velvet collar band (part of #8).
- 8) ~1901 Edwardian afternoon reception dress, bodice.
- 9) Late 19th century skirt, beige embroidered face fabric, brown lining fabric.
- 10) 1880-1900, dark blue and black jacquard pattern fabric.
- 11) Late 19th century, quilted bedspread, olive with pink stripes.
- 12) Three flag fragments from a painted silk 34-star flag from Lucy Ord Mason, Assession 5,771, catalog No. 156 (old No. 359).
- 13) A sample of an almost completely deteriorated silk lace fabric from an Edwardian Jacket (1906-1910) donated by the Atlanta Historical Society.

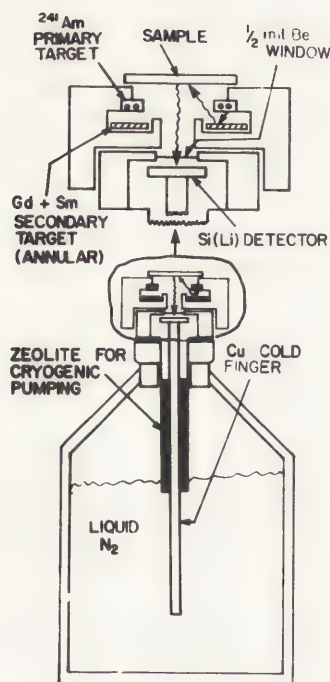


Fig. 1: X-ray fluorescence (XRF) apparatus.

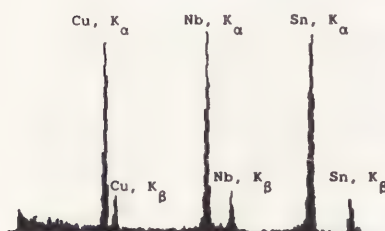


Fig. 2: XRF spectra of copper, niobium and tin standards ( $^{241}\text{Am}$  source, 768 full scale count, 113 sec).



Fig. 3: XRF spectra of iron standard ( $^{241}\text{Am}$  source, 384 full scale count, 40 sec).

### Test Methods

#### 1. Fiber Analysis

The fiber content of the fabrics was confirmed by microscopy. Two razor blades were inserted in a holder and clamped in place leaving 3 mm of the blades exposed and spaced 250  $\mu\text{m}$  apart [9]. The fabric to be examined was sliced at an angle of 45° to the weft and warp. The cut fibers were then scraped from the razor blades and placed on a slide covered with mineral oil. The birefringence of the fibers was then measured in a polarizing microscope. Silk fibers lying 45° to the crossed polars can be identified by their first and second order colors on a Michel-Levy scale of birefringence [10].

#### 2. Dye Analysis

The black fabrics were analyzed for the presence of logwood by the Schwappe technique [11]. The procedure consisted of sequentially extracting the dyes in ethanol, glacial acetic acid and ammonia and comparing the color of the solution and fiber to those of known dyes. In the case of silk, unlike wool or cotton, black fabrics are usually dyed with both logwood and tannin which makes the identification more difficult.

#### 3. Weighting Agent Analysis

The metallic elements in the fabric were identified by X-ray fluorescence (XRF) spectroscopy because it is a convenient, non-destructive method. Unfortunately, only qualitative results are available at this time.

The apparatus used was a Kevex Model 3000 with a Si(Li) detector and consists of a large dewar flask filled with liquid nitrogen (Fig. 1). A copper rod extends into the liquid nitrogen and is connected to a detector at the top. The copper cooling rod is required in order to reduce the molecular motion in the detector in order to increase its sensitivity. Each sample was placed on top of the detector and exposed to an excitation source of  $^{241}\text{Am}$  which excited in turn a secondary mode target of mixed Gd and Sm. The energies of the fluorescing photons were measured and counted for 60 sec (unless otherwise noted) and plotted automatically with an Apple IIc and NEC® PC-8023A-C printer. The plots were made with full scale ordinate counts of 192, 384 or 768. The energy range for all spectra was 0-30 keV.

The count versus energy curves for copper, niobium, tin and iron standards are shown in Figs. 2 and 3. The energy is plotted across the abscissa and the ordinant represents the number of photons emitted during the counting interval at each energy. Each energy is characteristic of a specific element. Unfortunately, organic vegetable additives cannot be detected by XRF.

### Results and Discussion

All the samples evaluated, including pipings and linings, appeared to be silk. The only exceptions were the green brocade fabric



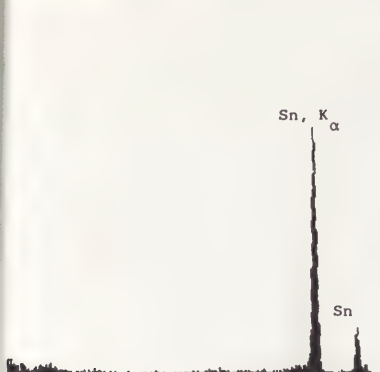


Fig. 4: XRF spectrum of late 19th or early 20th century wedding dress, sample 1 (768 full scale count, 60 sec).

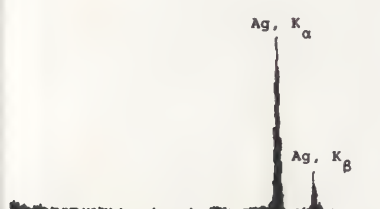


Fig. 5: XRF spectrum of late 18th or early 19th century pink fabric with beige binding and metallic embroidery, sample 5 (768 full scale count, 60 sec).

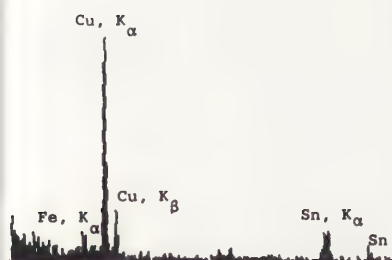


Fig. 6: XRF spectrum of late 19th century vest, sample 6 (192 full scale count, 60 sec).

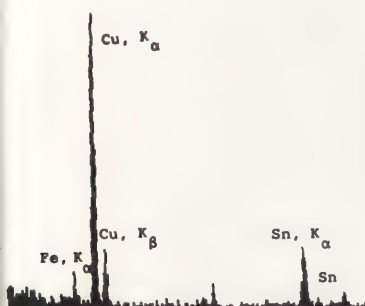


Fig. 7: XRF spectrum of black brocade front fabric of vest, sample 6 (192 full scale count, 60 sec).

(sample 4) in which some cotton may be present and a layer of fabric of cotton between the outer fabric and the lining of the Edwardian reception dress (sample 8). The spectrum of sample 1, a beige-white satin fabric, clearly shows the  $K_{\alpha}$  and  $K_{\beta}$  peaks of tin (Sn) which indicates the presence of traditional tin salts as weighting agents (Fig. 4). Sample 5 shows no signs of weighting in the pink fabric or in the beige binding. The metallic threads in the embroidery, however, were found to be silver (Fig. 5).

An interesting example of a garment consisting of a number of different components is sample 6, a vest from 1880-1890. This vest consists of an outer black brocade fabric with a black lining and a inner front panel of gold brocade lined with a gold fabric. In addition there was a black facing fabric around the armholes and waist.

This multicomponent vest when examined as a composite showed the presence of tin and at least one additional element (Fig. 6). After examining the individual components of the vest (Figs. 7-11), the new peaks were found to be particularly prominent in Figs. 7 and 8. The energies of the peaks suggested that they might be Cu and Fe, which was confirmed by the calibration standards shown in Figs. 2 and 3 and by longer exposures over a narrower energy range to verify the presence of iron. The black brocade fabric showed a spectrum containing tin, copper and iron (Fig. 7). The black lining of the upper vest layer contained both tin and iron (Fig. 8). The black facing around the armholes and waist showed a very small amount of iron and possibly tin above the background spectrum (Fig. 9). The gold face fabric of the two-component underneath layer contained tin (Fig. 10), while the gold lining of the under layer was not weighted (Fig. 11).

The presence of iron, particularly in black fabric, is not entirely unexpected. As discussed in the introduction, iron compounds are well-known weighting agents and are often used in conjunction with logwood for dyeing silk black [2,7,8]. Both copper sulphate and copper acetate are also known to be used in dyeing silk black with logwood [8]. This could explain the appearance of copper in the spectrum of sample 6, the black face fabric of the vest. All the black fabrics in sample 6 were found to be dyed with logwood and tannin.

Samples 7 and 8 were pieces from an Edwardian reception dress, dated around 1901. The collar piece (sample 7) consisted of a green pleated fabric containing no weighting agents, attached to a collar band of beige lining and black velvet. The beige lining on

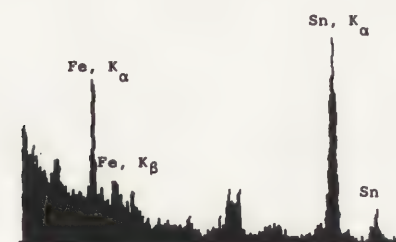


Fig. 8: XRF spectrum of black lining fabric of vest, sample 6 (384 full scale count, 600 sec).



Fig. 9: XRF spectrum of black facing fabric of vest, sample 6 (192 full scale count, 600 sec).



Fig. 10: XRF spectrum of gold face fabric of vest, sample 6 (192 full scale count, 60 sec).



Fig. 11: XRF spectrum of gold lining fabric of vest, sample 6 (192 full scale count, 60 sec).



Fig. 12: XRF spectrum of beige lining from Edwardian collar, sample 7 (192 full scale count, 60 sec).

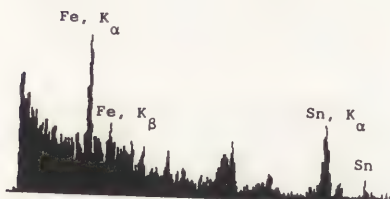


Fig. 13: XRF spectrum of black velvet band from Edwardian collar, sample 7 (384 full scale count, 60 sec).



Fig. 14: XRF spectrum of blue bow from collar, sample 7 (192 full scale count, 60 sec).



Fig. 15: XRF spectrum of gold bow from collar, sample 7 (192 full scale count, 60 sec).



Fig. 16: XRF spectrum of beige face fabric from Edwardian dress, sample 8 (192 full scale count, 60 sec).



Fig. 17: XRF spectrum of beige lining fabric from Edwardian collar, sample 8 (192 full scale count, 60 sec).

the band showed evidence of tin weighting (Fig. 12). The black velvet section showed a small amount of tin but a larger amount of iron (Fig. 13). Dye analysis showed logwood and tannin to be present in the black velvet fabric. A beige lace was attached to the green pleated section. No metallic weighting agents were detected in the lace. Tin was found, however, in the light blue and gold bows that were attached to the lace (Figs. 14 and 15). The bodice, to which the collar was attached, was highly degraded on the outside, and the spectrum showed tin to be present (Fig. 16). The lining also contained tin but had no visible signs of degradation, probably because it had less exposure to light (Fig. 17). The green strap used for attaching the front of the bodice together showed no evidence of tin.

The late 19th century skirt (sample 9) consisted of a highly degraded beige face fabric and a brown lining. The face fabric contained tin (Fig. 18) while the lining showed no metals present (Fig. 19).

None of the remaining samples indicated that any metal weighting agents were present. Dye analysis of the blue and black jacquard fabric (sample 10) which contained no weighting agents showed that the black dye was not logwood.

Although the peak heights are proportional to the concentration of the elements present in the exposed area, a quantitative relationship between photon-count and the amount of the element present in the fabric is difficult to determine. This relationship depends on such factors as fabric thickness, yarn twist, fabric construction, and surface contours. Because of these complications, XRF is currently being used only as a simple, efficient, non-destructive method of qualitatively determining types of weighting agents. Since the quantitative analysis of weighting agents in fabrics by XRF is difficult, other methods, such as atomic absorption spectroscopy, are likely to be more appropriate for quantitative analysis. Preliminary trials have been very promising.

Additional evaluations that are being made on these historic fabrics include atomic absorption spectroscopy to quantify the amount of weighting agent present, breaking strength, ammonia-nitrogen, and amino-nitrogen content. From these measurements it should be possible to gain an insight into the influence of weighting agents on the degradation mechanisms of silk. For example, if the interrelationships between strength, amino- and ammonia-nitrogen contents are found to differ for weighted and unweighted silks, it would suggest that different degradation methods might be operative. Controlled aging studies on weighted and unweighted contemporary silks would of course be necessary to confirm such conclusions.

### Conclusions

XRF has been found to be a simple, efficient and non-destructive method for quickly determining the presence of metallic weighting and mordanting agents in silk fabrics. It is unlikely to be suitable for quantitative measurements however. Preliminary studies indicate that quantitative measurements can be readily obtained using atomic absorption spectroscopy. A summary of the findings is presented in Table 1.



Fig. 18: XRF spectrum of beige face fabric from skirt, sample 9 (192 full scale count, 60 sec).



Fig. 19: XRF spectrum of brown lining fabric from skirt, sample 9 (192 full scale count, 60 sec).



Table 1: Weighting Agent Summary.

	Metals Present	Dye (black fabrics only)
<u>18th Century</u>		
Green brocade (sample 4)	-	
Pink fabric with metallic embroidery (sample 5)	Ag; not used as a weighting agent	
<u>1862</u>		
Three flag fragments (sample 12)	-	
<u>Late 19th or early 20th century (1880-1910)</u>		
Wedding dress (sample 1)	Sn	
Green fabric with satin stripe (sample 2)	-	
White fabric with piping (sample 3)	-	
Black vest (sample 6)	Sn, Fe, Cu	Logwood
Edwardian collar piece (sample 7)	Sn, Fe	Logwood
Edwardian dress bodice (sample 8)	Sn	
Brown skirt and lining (sample 9)	Sn	
Blue and black jacquard fabric (sample 10)	-	Not logwood
Quilted bedspread (sample 11)	-	
Silk lace from Edwardian jacket (sample 13)	-	

Of the thirteen samples examined, five were found to be weighted with tin, and the remaining eight contained no tin. In addition, one of the three components in sample 6 contained both iron and tin. One component contained iron, tin and copper and one contained a very small amount of iron and a trace of tin. Finally, one sample contained silver in an embroidery yarn, but no weighting agents were present.

It is perhaps of interest to note that the five samples (1,6,7,8,9) found to contain tin were all from garments attributed to the late 19th century or ~1901. Only one sample from an early 20th century garment (sample 13) did not contain tin. Neither of the 18th century fabrics (samples 4 and 5) contained tin nor did the three flag fragments. The three fabrics (samples 2, 3 and 10) and bedspread (sample 11) (late 19th or early 20th century) did not contain tin. The fabrics containing iron and copper were in fabrics that also contained tin (samples 6 and 7).

The four black fabrics in samples 6 and 7 all contained both tin and iron and were found to be dyed with logwood. The black sample which contained no metallic elements (sample 10) was not dyed with logwood.

Tin was patented as a mordant in 1748, but it was not until 1897 that a patent appeared teaching the use of tin as a weighting agent [7]. Weighting of silk with iron was practiced as early as 1630. It was not until the latter part of the 19th century, however, that tin was used as a weighting agent. These times would be consistent with our findings that all the fabrics weighted with tin were in garments from the late 19th or early 20th centuries. The fabrics containing tin appear more degraded than those without tin.

Further study will be necessary to quantify the extent to which tin accelerates degradation of silk fabric. Although the original condition of these fabrics is unknown, their original properties were likely to be similar to those of contemporary fabrics. Because the history of their treatment and exposure to light and heat since their manufacture is not known, the actual extent of damage caused by the weighting agents is uncertain.

#### Acknowledgments

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References

1. Tyler, A. G. "Survey of Silk Weighting," Text. J. of Australia, 1949, 24, 404-407, 464.
2. Bogle, M. M. "The Deterioration of Silks Through Artificial Weighting," Textile Conservation Center Notes, No. 11, Merrimack Valley Textile Museum, North Andover, MA (1979).
3. Harris, M. "The Photochemical Decomposition of Silk," Amer. Dyestuff Repr., 1934, 23, 403-404.
4. Roberts, N. M. and Mack, P. B. "A Study of the Effects of Light and Air on Unweighted and Tin Weighted Silk," Rayon Melland Text. Mon., 1936, 16, 102.
5. D'Olier, A. A. and Mack, P. B. "The Effect of Darkroom Storage on Unweighted and Tin Weighted Silk," Rayon Melland Text. Mon., 1936, 17, 49-53.
6. Yoshio, K. and Niki, E. "Oxidative Degradation," Aspects of Degradation and Stabilization of Polymers, Jellinek, H. H. G., ed., Elsevier Scientific Publishing Co., NY, 1978, 79-147.
7. Howitt, F. O. Bibliography of the Technical Literature on Silk, Hutchinson's Scientific and Technical Publications, London, 1952, 183-205.
8. Gandswindt, A. Dyeing Silk, Mixed Silk Fabrics and Artificial Silks, D. Van Nostrand, NY, 1921.
9. AATCC Technical Manual, The American Association of Textile Chemists and Colorists, Research Triangle Park, NC, 1986, 62, 63, 68.
10. Rochow, T. G. and Rochow, E. G. An Introduction to Microscopy by Means of Light, Electrons, X-rays or Ultrasound, Plenum Press, NY, 1978, 91-112.
11. Schweppe, H. "Identification of Dyes on Old Textiles," J. of Amer. Inst. of Cons., 1980, 19, 14-23.



## SUMMARY

A set of cotton fabrics was artificially aged at temperatures from 100 to 150 °C following treatment with sodium borohydride ( $\text{NaBH}_4$ ). Percent tear strength retention and degree of polymerization was measured and compared to a control set without treatment.

It was found that the borohydride treatment decreased the rate of degradation by about a factor of two. In addition, it is shown that tear strength is a good proxy for degree of polymerization, thus, greatly simplifying experimental procedures.

## TREATMENT OF CELLULOSIC TEXTILES WITH SODIUM BOROHYDRIDE

Ira Block\* and A. M. Roy

\*Conservation Scientist

Department of Textiles and Consumer Economics

University of Maryland

College Park, MD 20740, USA

## Introduction

Cotton cellulose converts to oxycellulose when exposed to atmospheric oxygen. Chemical reaction takes place in a non-specific manner (1) along the available surface of the molecules. Rowland (2) proposed that fibrous cellulosic materials are composed of fibrils containing (a) highly ordered, inaccessible internal surfaces, (b) less ordered partly accessible surfaces, and (c) readily accessible, disordered outer surfaces. It is only on the accessible surfaces that oxidative attack yielding carbonyl and carboxy species can occur. Thus, the less dense, non-crystalline regions are attacked first, followed by a slower attack on the more highly crystalline material.

A decrease in molecular weight may result from oxidation at the 1,4-glycosidic bond (1) or through beta elimination reactions (3). Scissioning of the polymer may occur as a random attack along the length of the molecule, which rapidly lowers the degree of polymerization (DP), or by an "unzipping" reaction whereby the end unit of the macromolecule is removed, leaving a reactive complex which can also detach from the main chain. This latter reaction can lead to large decreases in weight of material with little change in the DP of the remainder (4). The general scheme whereby cellulose is oxidized is shown in Fig. 1.

Since degraded celluloses are more crystalline than new celluloses (5 - 7), the disordered surface available for the formation of  $-\text{COOH}$  groups is constantly decreasing as the fiber ages. Furthermore, it has been shown (6, 8 - 11) that although the early stages of degradation support the formation of carboxy acids, these decay, and the major cause of cellulose degradation is the chemical reactions of the carbonyl groups ( $>\text{C}=\text{O}$ ) which are formed along with acids, but in greater quantity, when cellulose is oxidized.

The oxidation of cellulose is complex. Hydroxyl groups ( $-\text{OH}$ ) on the cellulose form both carboxyl and carbonyl groups, and these in turn, can be either oxidized or reduced to the other. Finally, the carboxyl groups decay away leaving the carbonyl groups to continue the degradation process. Thus, it can be understood why an alkaline treatment, intended to neutralize carboxyls, may not be effective for aged cellulose although, depending upon the reagent used, can be quite successful for new cellulose (12,13).

That carboxylic acid groups on the cellulosic chain play a minor role in the decay of the material is not surprising. As Davidson and Standing (14) and Davidson and Nevell (15) showed, acidic oxycelluloses are unstable because the carboxylic acids are converted to water-soluble, low-molecular-weight species. Thus, in old cellulosic textiles, the acidic species are removed from the fabric upon washing, and deacidification is not necessary (12). Kerr et al. (16, 17) and more recently Hackney and Hedley (18) have provided independent evidence of the correctness of this view.

If the carboxylic acids on the cellulosic chain are not the major cause of the thermooxidative decay of old cellulosic textiles, one must consider the carbonyl species, particularly the aldehydes on the  $\text{C}_2$  and  $\text{C}_3$  carbons. Nikitin (19) noted that "the primary autoxidation process is a reaction of molecular oxygen with aldehyde groups, which initiates a chain reaction resulting in more profound changes and decomposition of the molecule." Lewin, et al (20) and Jullander (21) have also noted that the carbonyl species are the cause of discoloration in cellulose. Thus, removal of aldehydes and ketones should greatly delay the degradation of cellulose by restoring the fiber to a condition closer to its original state. Further studies have shown that carbonyl groups are responsible for color reversion and brightness reversion (21,22).

In recent years, conservators have studied the use of reducing agent bleaches on paper. Although oxidative bleaching agents have a good ability to remove stains from artifacts and the brightness gained is excellent, they have been shown to be the cause of significant oxidation of fibers (23). Rapson and Hakim (24) have

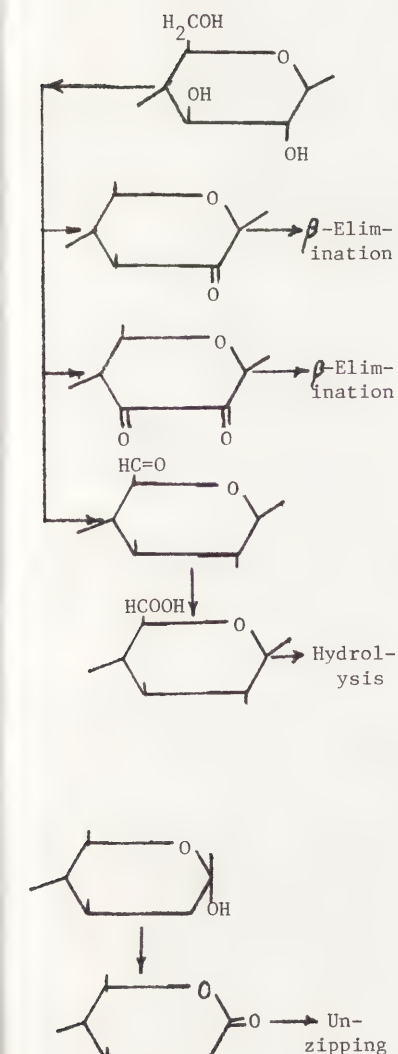


Figure 1: Generalized Oxidation of Cellulose Leading to Chain Splitting and Unzipping.



shown that color reversion can be reduced if carbonyl is reduced to hydroxyl with  $\text{NaBH}_4$ . Burgess (35) noted a decreased rate of yellowing of rag papers following  $\text{NaBH}_4$  treatment, while Head demonstrated that the reducing agents reverse the degradative effects of oxidative bleaching; presumably, because of conversion of the carbonyl groups in cellulose to primary alcohol groups (25, 26). Thus, it has been shown that the use of alkali borohydrides, such as  $\text{NaBH}_4$ , gives excellent brightness gain, minimal degradation and good color reversion properties in paper conservation. Burgess (22) also notes that BH's have been described as being able to increase fibers' resistances to acid hydrolysis, oxidation, alkali and the effects of near UV radiation. These properties are related to BH's specific reduction of the carbonyl functional groups which are some of the degradation products characterizing old, deteriorated fibres.

Sodium Borohydride ( $\text{NaBH}_4$ ) reduces water to hydrogen according to the equation (27):



Although the mechanical action of the hydrogen gas evolution may damage degraded objects (28), this can be reduced by using lower reagent concentrations for longer treatment times and by washing the object well beforehand (27). It has been reported that the presence of cations such as calcium, barium and magnesium have a positive effect on the efficiency of sodium borohydride as a reducing agent (21,29), possibly due to the change in pH of the solution caused by the addition of the salts. Besides  $\text{NaBH}_4$ , potassium, tetramethylammonium ( $(\text{CH}_3)_4\text{NBH}_4$ ) and tetraethylammonium borohydride ( $(\text{C}_2\text{H}_5)_4\text{NBH}_4$ ) have also been used as reducing agents, but they seem to be less effective than the sodium salt (22,30,31).

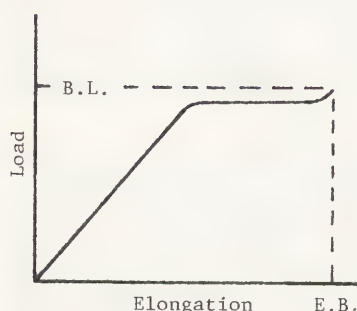


Figure 2: Load Elongation Curve Showing Breaking Load (B.L.) and Extension at Break (E.B.).

Measurements of the mechanical properties of textiles and paper are often used to assess the integrity of the fibers from which they are made (32 - 37). Usually, the investigator assumes, sometimes explicitly, that the rate of change in mechanical properties is directly related to the rate of chemical change. In this work we have considered tensile and tear testing of the cloth and viscosimetric measurements of fiber degree of polymerization for characterizing the system.

Fiber, yarn, and fabric may be subjected to tensile testing, in which a load is applied to the material and both the load and extension are measured (38). A typical load/elongation curve is shown in Fig. 2 for a fabric. The major features of this curve are the almost linear initial portion (elastic region), the slope of which is called the elastic modulus, the plateau beyond the yield point (plastic region) and the break point. The area under the curve is the "energy to rupture," and is the work required to break the sample.

Of major interest in the study of textile degradation are changes in (1) the elastic modulus, which indicate embrittlement, (2) the breaking load, which shows scissioning of polymer, (3) the energy to rupture, which indicates loss of toughness and (4) the elongation at break, another measure of polymer chain scission.

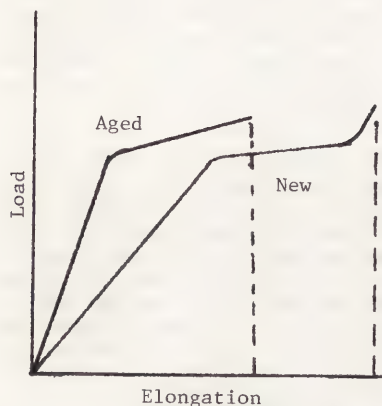


Figure 3: Typical Load-Elongation Curves for New and Aged Cloths.

Initial measurements of tensile strength, elongation at break and energy to rupture were erratic. It was found that breaking load could either increase or decrease at short baking times, and that the results were irreproducible. Furthermore, even for those samples in which breaking load and elongation decreased, energy to rupture could increase. This last phenomenon is explained by examination of Fig. 3. Here both elongation-at-break and breaking load have decreased upon aging, but because the sample has become more brittle the modulus has increased and, thus, the energy to rupture has remained constant; even though the fiber has been degraded. Similar effects can be obtained when measuring breaking load and elongation at break.

This problem led to an investigation of the correlation between tensile and tear testing. The results, reported previously (31), showed that tensile strength was insensitive to fabric age until the tear strength had fallen to about 70% of the initial value. For cloths degraded beyond this point, a linear relationship exists between tensile and tear strengths. Furthermore, as noted by Taylor (39), "... in contrast to the role of tensile strength, tearing strength is directly involved in the assessment of serviceability" of cotton fabrics. Thus, because tear strength is more closely related to the performance of the cloth in actual use, and because it proved to be more sensitive to treatment of the fabric than tensile strength, mechanical testing is reported in terms of this parameter.



Another measure of the chemical state of a cellulosic textile material is the color of the fabric, since aging of cellulose leads to a gradual darkening (20) of the cloth. It was noted in previous work (13) that deacidification did not change the rate of discoloration of artificially aged cloth, but that treatment with either sodium borohydride or tetramethylammonium borohydride greatly improved the color of artificially aged cotton cloth to the extent that it would take centuries at ambient condition for the treated fabric to degrade to the color of untreated material (31).

### Experimental

The viscosity-average degree of polymerization (DP) was found by grinding cloth specimens to pass a 20-mesh sieve in a Wiley Mill, dissolving the linters in CUENE and measuring the efflux time of the solution in a capillary viscometer.

Three sections were taken from each fabric sample. The specimens were individually ground, and those fibers which passed through the sieve into a nitrogen-flushed glass vial, were tested. Ground fibers were stored in the dark prior to testing. Storage times did not exceed one week.

Fibers were dried as per AATCC 82-1975 (40), in which the fiber is placed on an elongated aluminum foil carrier and placed in a dessicator above a Petri dish containing 25 ml of concentrated sulfuric acid as dessicant. Drying overnight provided a specimen moisture content of 2% or less.

Cupriethylenediamine Hydroxide, 1.0 M (CUENE)  $\text{Cu}(\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2)_2(\text{OH})_2$  was supplied by Reagents, Inc., Charlotte, North Carolina. CUENE solutions were prepared by placing 500 ml of the 1.0M reagent in a one-liter volumetric flask and filling with deionized water to make a 0.5M solution. Nitrogen gas was bubbled through the 0.5M solvent to reduce the reduction of the copper by atmospheric oxygen to a minimum. CUENE is an unstable alkaline solvent, which should be refrigerated during storage to prevent its disassociation and precipitation of copper.

Dried specimens of various weights were weighed and placed in a clean dry-nitrogen flushed 125 ml Erlenmeyer flask followed by the addition of 30 ml of 0.5M CUENE solution. Oxygen was displaced by a steady flow of dry nitrogen gas at 1 psi. Maintenance of the nitrogen atmosphere was accomplished by flowing the gas through a fine bore glass tube inserted in the rubber stopper sealing the flask. A second hole in the stopper held a pipette, through which CUENE reagent could be added and the polymer solution removed. The flask opening was sealed with sheet paraffin wax stretched across its mouth and across the tip of the glass tube. The sealed flask containing the polymer solution was placed in a constant temperature bath at 25°C for one hour and slowly shaken.

Calibrated, size 50 and 100 Cannon-Ubbelohde Four-Bulb Shear Dilution type viscometers were used in this study. The intrinsic viscosities of the specimens were calculated from the following multiple regression model.

$$Y_i = B_0 + B_1X_{i1} + B_2X_{i2} + e_i$$

where:

- $Y_i$  = reduced viscosity
- $B_0$  = intrinsic viscosity
- $X_{i1}$  = shear rate,
- $B_1$  = shear rate coefficient estimate
- $X_{i2}$  = concentration, and
- $B_2$  = concentration coefficient estimate.

The intrinsic viscosity  $[\eta]$ , obtained at the intercept of the multiple regression equation is related to the viscosity number average degree of polymerization, by the Mark-Houwink equation:

$$[\eta] = K \times (\text{DP})^{\alpha}$$

where: the constants  $K = 0.017$  and  $\alpha = 0.80$  and  
 $\text{DP}$  = number average degree of polymerization.

### Results

It has been shown (41) that for polymers which degrade by first order or pseudo first-order kinetics one may follow the decrease in degree of polymerization by the equation

$$1/(\text{DP}) - 1/(\text{DP})_0 = kt$$

where : DP = the degree of polymerization at time  $t$ ,  
 $DP_0$  = the initial degree of polymerization, and  
 $k$  = the first-order rate constant.

The viscosity-average DP was determined for a number of fabric samples baked at temperatures between 100 and 150 °C. A typical plot of  $1/DP - 1/DP_0$  vs Baking Time is shown in Fig. 4. The model predicts that the plot should be a straight line with positive slope. However, the results show an initial rapid degradation which progresses into a final, slow loss in  $DP_v$ . This behavior may be explained on the basis of Rowland's model for cotton cellulose (2) described above. In the initial period, the more disoriented regions are rapidly degraded. The slow degradation rate at longer baking times shows the degradation of the highly oriented regions.

Examination of the sodium borohydride-treated (□) and water-washed (#) specimens reveals that less loss in DP has occurred for the treated specimens, and that the shapes of the curves for the treated and untreated materials are essentially the same.

Pseudo first-order rate constants were determined by linear regression of the short- and long-term degradation curves at baking temperatures of 100, 120, 140 and 150 °C for both treated and untreated fabrics. The results of this work, and previous results on tear strength measurements (31), are given in Table I.

Treatment of cotton fabric with 0.03M sodium borohydride solution at 25°C for approximately 20 minutes prior to baking at various temperatures reduced the rate of degradation by about a factor of 2 (1.94 0.59) in the short term. In the long run (when we are all dead) the ratio drops to 1 due to the loss of efficacy of the treatment and the reformation of carbonyl and carboxyl species. This indicates, as one would expect, that the treatment is not permanent.

The physical strength of textile fabrics is affected by the degree of polymerization (38). In this study, the correlation between DP and tear strength was investigated. The results of long-term and short-term data at the different temperatures were analyzed. The overall coefficient of determination,  $R^2$ , was found to be 0.88.

The results of this study clearly indicate that a sodium borohydride reduction treatment will reduce the rate of degradation of cellulosic fibers and also improve color. In addition, fabric tear strength may be used as a good proxy for degree of polymerization, thus, greatly simplifying the experimental determination of degradation rate.

#### References

1. Peters, R. H., Textile Chemistry: Vol. I, Elsevier Publishing Co., New York, 1963.
2. Rowland, S. P., "The Mechanism of Durable Press," Textile Chemist and Colorist, 4 204-212 (1972).
3. Peters, R. H., Textile Chemistry: Vol. III, Elsevier Publishing Co., New York, 19.
4. Nevell, T. P. and S. H. Zeronian (Eds.) Cellulose Chemistry and Its Applications, Ellis Horwood Ltd., Chichester, 1985.
5. Berry, G. M., S. P. Hersh, P. A. Tucker and W. K. Walsh, Reinforcing Degraded Textiles: Part I, Preservation of Paper and Textiles of Historic and Artistic Value, Advances in Chemistry Series (ACS) No. 164, ACS Washington, D.C., 228-248 (1977).
6. Kleinert, T. N. and D. Dioszagi and R. M. Dlouhy, "Alkali Solubilities of Cellulose Materials: 1. Dissolving Pulps," Svensk Papperstidn 62 834 (1959) and 62 863 (1959).
7. Berkley, E. E., "The Effect of Long Term Storage on Cotton" Textile Research Journal 27 171-172 (1957).
8. Wilkie, J. B., Laundry "Winter Damage," National Bureau of Standards Research Journal, 6 593 (1931).
9. Shafizadeh, F., Pyrolysis and Combustion of Cellulosic Materials, in 'Advances in Carbohydrate Chemistry,' M.L. Wolfrom and R.S. Tipson, Eds., Academic Press, New York, 1968.



10. Block, I., The Effect of an Alkaline Rinse on the Aging of Cellulosic Textiles: II, A paper read at the Ninth Annual Meeting of the AIC, Philadelphia, PA, 1981.
11. Hebeish, A., A. T. El-Aref and E. A. El-Alfi, "Effect of Short Thermal Treatment on Cotton Degradation," Journal of Applied Polymer Science 23 453-462 (1979).
12. Block, Ira, The Effect of an Alkaline Rinse on the Aging of Cellulosic Textiles: Part IV, Science and Technology in the Service of Conservation, 96 - 99, IIC, London, 1982
13. Block, Ira, The Effect of an Alkaline Rinse on the Aging of Cellulosic Textiles: Part II, JAIC, 22(1) 25-36 (1982).
14. Davidson, G. F. and H. A. Standing, The Auto-hydrolysis of Acidic Oxycelluloses, Journal of the Textile Institute, 42 T141-T144 (1951).
15. Davidson, G. F. and T. P. Nevelle, The Acidic Properties of Cotton Cellulose and Derived Oxycellulose: Parts I-VI, Journal of the Textile Institute, 39 T59-T129 (1948).
16. Kerr, N., S. P. and P. A. Tucker, Physical Changes of Alkaline-Buffered Cotton Fabric, Preprints: ICOM 7th Triennial Meeting, Copenhagen, 1984.
17. Kerr, N., S. P. Hersh, P. A. Tucker, and G. M. Berry, Reinforcing Degraded Textiles: Effect of Deacidification on Fabric Deterioration, ACS Symposium Series No. 95 357-369, ACS, Washington, DC, 1979
18. Hackney, S. and G. Hedley, Linen Canvas Artificially Aged, Preprints: ICOM 7th Triennial Meeting 16 - 21, Copenhagen, 1984.
19. Nikitin, N. I., "The Chemistry of Cellulose and Wood," J. Schmorak Trans., Israel Program for Scientific Translations, Jerusalem, 1979.
20. Albeck, M. A., J. A. E. Ben-Basset and M. Lewin, The Yellowing of Cotton Cellulose: Parts I-III, Textile Research Journal, 35 836-843 and 935-986 (1965).
21. Jullander, I., Borohydride Reduction of Pulps, Proceedings Second Conference, Cellulose Research Institute, Syracuse, New York, 80-109 (1959).
22. Ott, E., Cellulose and Cellulose Derivatives: High Polymer Series, Volume V, New York, Interscience Publishers, Inc., 1943.
23. Burgess, H. D., The Bleaching Efficiency and Colour Reversion of Three Borohydride Derivatives, Preprints: The American Institute for Conservation of Historic and Artistic Works, Tenth Annual Meeting, Milwaukee, Wisconsin, 40-48, 1982.
24. Hon., D. N. S., Yellowing of Modern Papers, Preservation of Paper and Textiles of Historic and Artistic Value II, ACS No. 193, ACS, Washington, D.C., 119-141 (1981).
25. Head, F. S. H., The Reduction of the Aldehyde Groups in Periodate Oxycelluloses by Sodium Borohydride, Journal of the Textile Institute, 46, T400-T406 (1955).
26. Head, F. S. H., The Reduction of the Aldehyde Groups in Hydrocelluloses by Sodium Borohydride, Journal of the Textile Institute, 46, T584-T586 (1955).
27. Gaylord, N. G., Reduction with Complex Metal Hydrides, Interscience Pub. Inc., New York, 1956.
28. Hey, Margaret, Paper Bleaching: Its Simple Chemistry and Working Procedures, The Paper Conservator, 2, 10-23 (1977).
29. Schlesinger, H. I., H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra, and E. K. Hyde, Sodium Borohydride, Its Hydrolysis and Its Use as a Reducing Agent and in the Generation of Hydrogen, Journal of the American Chemical Society, 75, 215-219 (1953).

30. Nevell, T. P. and S. H. Zeronian, The Effect of Periodate Oxidation and of Subsequent Borohydride Reduction on the Tensile Strength of Cotton, Journal of the Textile Institute, 53 T90-T93 (1962).
31. Block, Ira and H. K. Kim, Accelerated Aging of Cellulosic Textiles at Different Temperatures: The Effect of Tetrahydriodoborate Reduction, 411-426, ACS No. 212, ACS, Washington, D.C., 1986.
32. Arney, J. S. and A. J. Jacobs, "Accelerated Aging of Paper," Tappi 62, 89-91 (1979).
33. Graminski, E. L., E. J. Parks and E. E. Toth, The Effects of Temperature and Moisture on the Accelerated Aging of Paper, ACS Symposium Series No. 95 24, ACS Washington, D.C., (1979)
34. Mendenhall, G. D., G. B. Kelly, and J. C. Williams, The Application of Several Empirical Equations to Describe the Change of Properties of Paper on Accelerated Aging, Preservation of Paper and Textiles of Historic and Artistic Value II, ACS No. 193, 177 - 191 ACS Washington, D.C., (1981).
35. Morton, W. E. and J. W. S. Hearle, Physical Properties of Textile Fibers, London, The Textile Institute, 1975.
36. Van Wazer, J. R., Viscosity and Flow Measurement, Interscience Publishers, Inc., New York, 1963.
37. Cardamone, J. M. and Peter Brown, Evaluation of Degradation in Museum Textiles Using Property Kinetics, ACS 212, 41 - 76, ACS, Washington, D.C., 1986
38. Taylor, H. M., "Tensile and Tearing Strength of Cotton Cloths," Journal of the Textile Institute Transactions 50 T161 - T188 (1959)
39. American Association of Textile Chemists and Colorists, Fluidity of Dispersions of Cellulose From Bleached Cotton Cloth, AATCC Test Method 82-1975, American Association of Textile Chemists and Colorists Technical Manual, Research Triangle Park, NC, 1975.

TABLE I  
Degradation Rate of Cotton Fabric

		Temperature (°C)		
	100	120	140	150
By Degree of Polymerization (DP)				
Untreated Short Term	0.10	2.80	1.77	4.25
Treated Short Term	0.07	1.45	0.64	2.61
By Tear Strength Retention (TSR)				
Untreated Short Term	0.23	4.97	3.27	10.1
Treated Short Term	0.18	1.80	1.11	3.48
By D.P.*				
Untreated Long Term	0.04	0.16	1.37	1.14
Treated Long Term	0.03	0.20	1.58	1.09
By TSR*				
Untreated Long Term	0.11	0.74	2.56	5.01
Treated Long Term	0.08	0.25	1.02	2.62

$$1/(DP)_O - 1/(DP) = 0.5 \times [1/(TSR)_O - 1/(TSR)]$$

\*The differences are not significant at the 0.05% level.



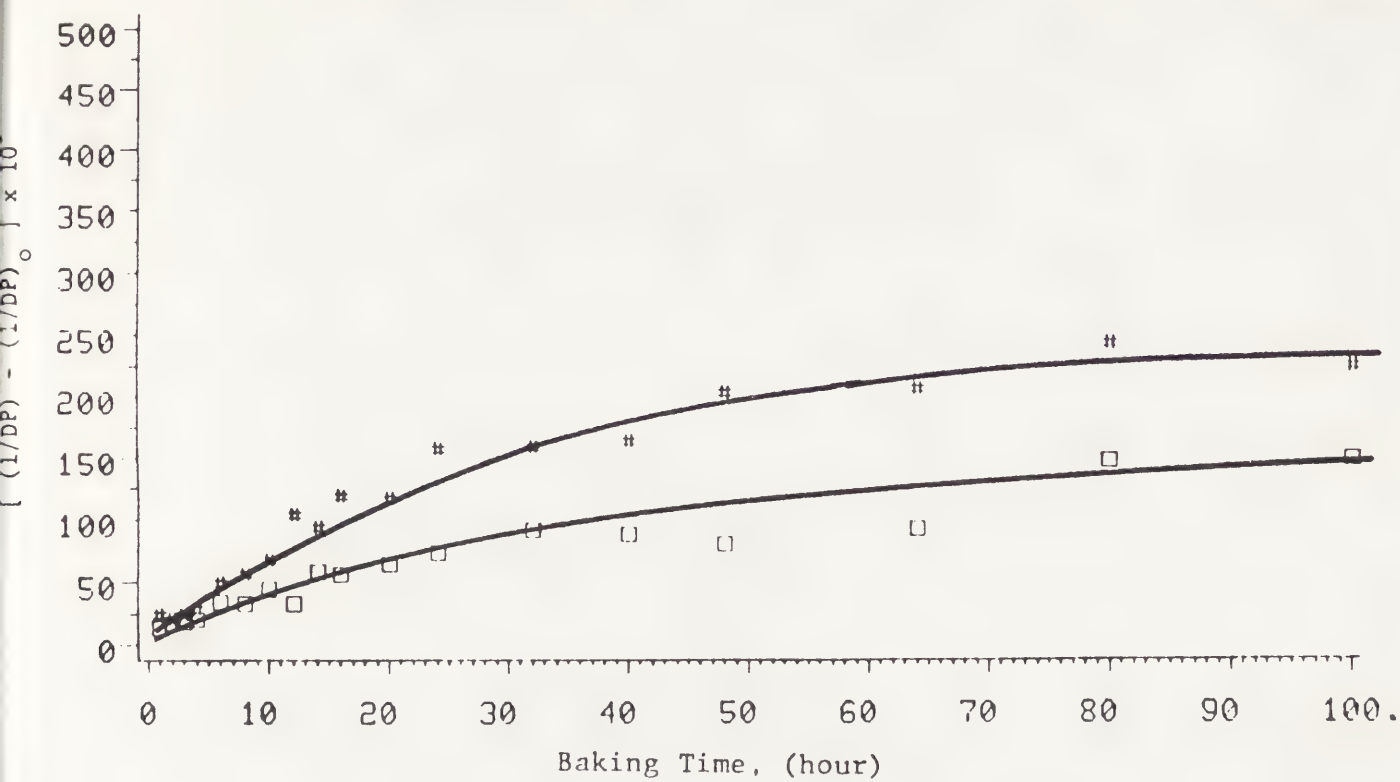


Figure 4: Depolymerization of Treated ( □ ) and Untreated ( # ) Cotton Fabric at 150°C.





## SUMMARY

The thermodynamic state of water adsorbed by cellulose was considered over a wide range of temperatures and water sorption. A two-dimensional virial equation of state model was employed, and literature data were analysed by computer to identify the properties of the water-cellulose system. Data are also given for more weakly interacting and non-swelling sorbates. At low surface coverage, the compressibility factor ( $Z$ ) exceeds 1, showing sorbate-cellulose interactions, and reaches a maximum. Past this point the decrease of  $Z$  shows the increasing predominance of interactions between adsorbed layers, until bulk liquid properties are reached. This analysis indicates some differences between the physical state of the water-cellulose system at standard conditions (23°C and 50% RH) and that prevailing at 105°C, used in the artificial ageing. Ageing with higher values of RH is more significant; this paper suggests their upper limits.

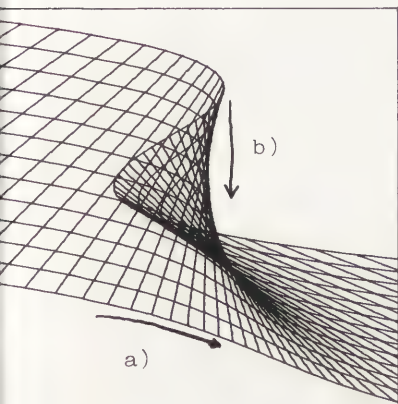


Fig.1. A walk over a continuous (a) and discontinuous (b) thermodynamic surface.

A TWO-DIMENSIONAL EQUATION OF STATE OF WATER ADSORBED ON THE SURFACE OF CELLULOSE: A TOOL TO BETTER UNDERSTAND THE ARTIFICIAL AGEING OF CELLULOSIC MATERIALS.

Paolo Calvini

Istituto Centrale per la Patologia del Libro  
76, via Milano, 00184 Roma Italy

### I) Introduction

The purpose of accelerated ageing of cellulosic materials is to reproduce the effects of natural ageing, chemically and physically. It is well known that paper and textiles deteriorate faster at increased temperatures, but there has been much discussion about the most meaningful conditions for artificial ageing: "Dry" or "moist" ageing? "Constant" or "cycling" conditions? This preliminary paper suggests some answers to these questions, but does not completely resolve the problem.

Let us forget for the moment the chemical aspects of reactions that take place at increasing values of temperature and humidity, and concentrate our attention on the physical aspects of ageing. We can imagine artificial ageing as a walk over a thermodynamic surface: such a walk may be continuous (Fig.1,a) or discontinuous (Fig.1,b) owing to a phase transition. The second condition is characteristic of real gases, but what about water adsorbed on the surface of cellulosic materials?

For a complete picture we need a good deal of information, such as experimental measurements of specific heats, specific volumes, conductance and dielectric properties, as well as X-ray analyses, IR studies, adsorption isotherms, NMR analyses and so on, all over a wide range of temperatures. Owing to the experimental difficulties, such data are often lacking in the literature, but all the studies of which we are aware show a common central theme: the role of water in the behaviour of cellulosic materials.

It is well known that under conditions of low relative humidity (RH) the water molecules are firmly bonded at the surface of cellulose until a monolayer is reached, and that with an increase in RH there is a decrease in water-substrate interactions, while the structure of water itself reaches the properties of bulk liquid, with the characteristic cluster-monomer equilibrium (1).

To react with cellulosic materials, the degrading agent must either pass through that sheath of water or activate the reactivity of water itself towards the substrate. So, before planning our experiments on artificial ageing, we must know the thermodynamic correspondence between the state of adsorbed water at normal and higher temperatures, as well as throughout the entire range of RH. As we lack even the fundamental calorimetric analyses (as mentioned above), we may bypass the difficulty via the equation of state of adsorbed water.

### II) Two-dimensional equation of state

Following Lewis and Randall (2), we may say that "there is every theoretical reason to expect a two-dimensional perfect gas to follow the equation  $\pi \tilde{A} \approx RT$  and to have other properties analogous to those of a three-dimensional perfect gas." Here,  $\pi$  is a two-dimensional pressure (say the difference between the surface tension  $\sigma^0$  of the clean substrate and  $\sigma$  of the surface with the adsorbate:  $\pi = \sigma^0 - \sigma$ ) and  $\tilde{A}$  the area per mole of adsorbed gas.

Real gases show significant deviations from this equation of state, even at low vapour pressure ( $P/P^0$ ). If the adsorption process can be considered as reversible, and with the simplification of a constant surface area ( $A$ ), we may write the Gibbs adsorption equation as a function of the amount of adsorbed water ( $n$ )

$$\frac{\partial \pi}{\partial n} = \frac{RT}{A} \frac{\partial \ln(P/P^0)}{\partial n} \quad [1]$$

and correlate eq.1 with the adsorption isotherms, beginning with the virial equation, the theoretical grounds for which have been well established (3), i.e.

$$\ln(P/P^0) = \ln(n) + \sum_{j=1}^M c_j n^{j-1} \quad [2]$$

The first coefficient is related to the limiting value at  $P/P^0 \rightarrow 0$  (Henry's law). Differentiation of eq.2 and integration of eq.1 between 0 and  $n$  gives

$$\frac{(\pi - \pi^0)A}{RT} = n + \sum_{j=1}^M \frac{j-1}{j} c_j n^j \quad [3]$$

$\pi^0$  being the value at zero surface coverage  $\pi^0 = \pi^v$  and, as the three-dimensional case,

$$\frac{(\pi - \pi^0)A}{nRT} = 1 + \sum_{j=1}^M \frac{j-1}{j} c_j n^{j-1} \quad [4]$$

The right term of eq.4 is the so-called compressibility factor ( $Z$ ).

In this paper, the  $C_j$  parameters were determined from literature isotherms by applying Davidon's algorithm (4), in order to minimize the function

$$f(c_1, c_2, \dots, c_M) = \sum \frac{[\ln(P/P^0) - f(n_i)]^2}{\ln(P/P^0)} \quad [5]$$

where  $f(n_i)$  is the right term of eq.2. Computations were made by a personal computer using an iterative technique and carried out until a minimum value of  $\chi^2$  was reached. Davidon's algorithm fails, of course, at  $n=0$  and at  $P/P^0=1$ . In practice we found it is difficult to interpolate the upper values of  $P/P^0$  ( $>90\%$ ) with eq.2; we need several coefficients (from 5 to 7) and thus a good deal of experimental points (5). Therefore we are studying other isotherm equations, to take into account the variations of surface area during the adsorption process.

### III) Analysis of some isotherms from the literature

#### a) Swelling and non-swelling sorbates

Whereas the literature abounds with investigations of the interaction between cellulosic materials and water, very few studies on the isotherms of non-aqueous vapours have been reported. In the present paper, therefore, only four sorbates were chosen:

n-decane	a non-swelling agent, weakly interacting with cellulose (data from ref.6)
dioxane	non-swelling and acceptor-only of H-bonds from cellulose (data from ref.6)
butan-1-ol	non-swelling and acceptor/donor of H-bonds (data from ref.6)
water	swelling and strongly interacting with cellulose (data from ref.7)

As shown in Fig.2, a general feature of these sorbates is a positive deviation from ideal gas law, at least from low to moderate values of  $P/P^0$ . The compressibility factor  $Z$  reaches a maximum at values close to the BET (8) monolayer completion. The height of this maximum (see Tab.I) is consistent with surface-sorbate attraction (which decreases in the order water  $>$  butan-1-ol  $>$  dioxane  $>$  n-decane). As  $P/P^0$  increases the attractive forces between sorbate molecules produce a decrease of  $Z$ , which recrosses 1, as also depicted in Tab.I.

Dioxane shows an anomalous behaviour, joined to a lower value of  $P/P^0$  at which  $Z=Z(\max)$ . There is the possibility that a specific orientation of the dioxane molecule permits very favourable hydrogen bonding to the cellulose lattice at low coverage (6) and that the structure persists well into the successive layers (inflection point of Fig.2,B).

An interesting aspect of the model developed in this paper is depicted in Fig.3, which is related to the mesitylene adsorbed on dry cellulose (Fig.3,a) and cellulose conditioned at 96% RH (Fig.3,b); data are taken from ref.9. When the adsorption takes place

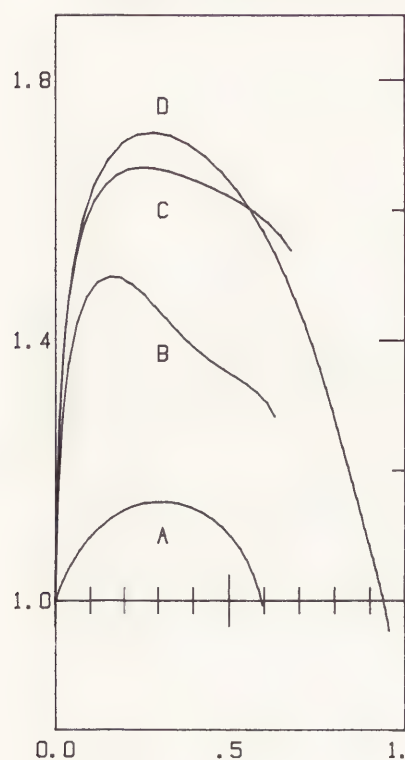


Fig.2. Compressibility factor  $Z$  vs.  $P/P^0$

- A) n-decane
- B) dioxane
- C) butan-1-ol
- D) water

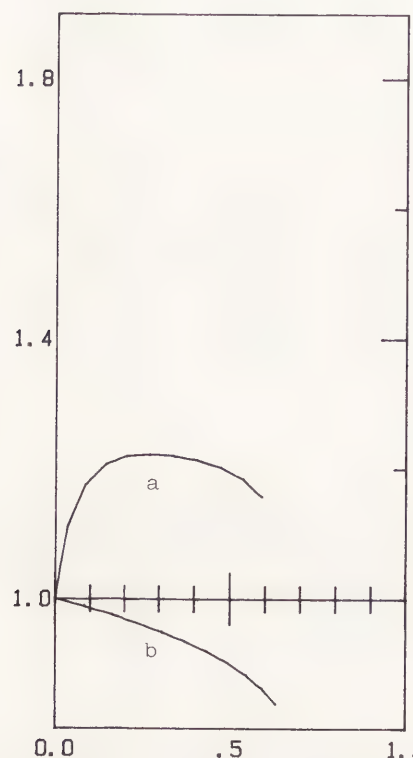


Fig.3. Compressibility factor  $Z$  vs.  $P/P^0$

- a) mesitylene adsorbed on dry cellulose
- b) on moist cellulose



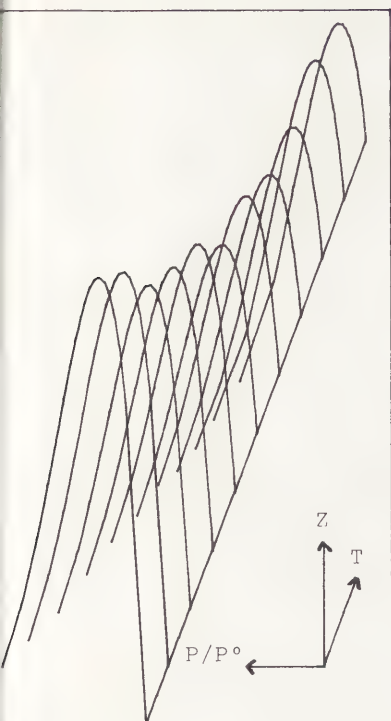


Fig.4. Compressibility factor  $Z$  vs. temperature  $T$  and relative humidity  $P/P^\circ$  of water adsorbed on the surface of cellulose.

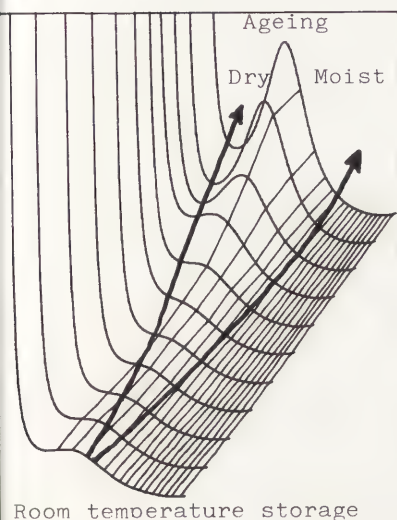


Fig.5. Two walks over a thermodynamic surface.

over a liquid-like surface of pre-adsorbed water, the compressibility factor of mesitylene is always negative and does not show any monolayer completion.

#### b) Influence of temperature on the compressibility factor

The application of eq.4 to Urquhart and Williams' data (10) on a mercerized cotton-water vapour system is shown in Fig.4 and Tab.II. Deviations from ideal behaviour are lower at higher temperatures, and  $Z$  value at  $110^\circ\text{C}$  is close to the value of  $n$ -decane at  $30^\circ\text{C}$ , indicating a weak interaction of water with the cellulose lattice.

#### IV) Application to artificial ageing

The values of  $P/P^\circ$  in which  $Z=Z(\text{max})$  and  $Z$  recrosses 1 seem to be transition points from monolayer to multilayer and from multilayer structure to bulk liquid.

Since the water structure plays an important role in cellulose conservation and degradation, the "walk over the thermodynamic surface" mentioned at the beginning of this paper ought not to cross these limits, as depicted in Fig.5. And not only for artificial ageing, but also for conservation purposes.

#### V) Model confirmation and conclusions

Although only a first approximation (due to the simplifying hypotheses introduced), the model depicted in this paper allows us to recognize some characteristics of the cellulose-water system. Not only does it identify the value of the water monolayers as a "transition point" (which one may calculate more simply by means of the BET (8) equation), but this model also identifies an upper limit of  $P/P^\circ$  in which the structure of water layers "collapses" into bulk liquid.

This behaviour has been confirmed by various experimental and theoretical studies. Some authors (11,12) observed variations of spin-lattice and spin-spin relaxation times at values close to the Tab.II points in HR-NMR analysis of water adsorbed on the cellulose surface. A different theoretical approach (cluster integrals) shows (13) that at low humidities the water-polymer contacts are favoured, while the size of clusters rises slowly up to 70-85% of RH and rapidly from this point on.

Thus, the behaviour of the water-cellulose system needs further investigations, covering a wide range of temperatures, via calorimetric analyses. But such data are lacking in the literature, while the wide-spread calculation of  $\Delta H$  by the integration of Clausius-Clapeyron equation is, in my opinion, too rough an approximation. The problem of artificial ageing remains, therefore, open for further research.

Tab.I

(Influence of sorbates on the compressibility factor  $Z$ )

Sorbate	Temp. ( $^\circ\text{C}$ )	Maximum value of $Z$		$P/P^\circ$ at which $Z$ recrosses 1
		$P/P^\circ$	$Z$	
$n$ -decane	30	0.30	1.15	0.58
dioxan	25	0.17	1.50	(0.75)
butan-1-ol	35	0.25	1.67	(0.96)
water	24.6	0.29	1.73	0.94

Notes: Data between brackets were extrapolated from Fig.2.

$Z$  was expressed in arbitrary units. The actual value depends on the integration constant and on the variables of eq.4.

Experimental data of water from ref.7.

Experimental data of other compounds from ref.6.

Tab.II

(Influence of temperature on the compressibility factor Z of water adsorbed by mercerized cotton)

Temp. (°C)	Maximum value of Z		RH at which Z recrosses 1
	RH	Z	
10	0.30	1.72	0.95
20	0.31	1.64	0.93
30	0.30	1.52	0.90
40	0.31	1.46	0.88
50	0.34	1.34	0.85
60	0.34	1.29	0.81
70	0.34	1.24	0.80
80	0.34	1.19	0.77
90	0.33	1.20	0.75
100	0.35	1.21	0.77
110	0.35	1.19	0.76

Notes: Z was expressed in arbitrary units (see Tab.I).  
Experimental data from ref.10.

## REFERENCES

- 1) For a simple review see: R.J.Dobbins, TAPPI 53(12),2284 (1970)
- 2) G.N.Lewis and M.Randall, "Thermodynamics" McGraw-Hill Company (1961)
- 3) W.A.Steele, "The Interaction of Gases with Solid Surfaces" Pergamon, Oxford (1974)
- 4) W.C.Davidon, Math.Prog. 9,1 (1975)
- 5) J.Cortes et al., JCS, Faraday Trans.I 79,1833 (1983)
- 6) R.Tremaine and D.G.Gray, JCS, Faraday Trans.I 71,2170 (1975)
- 7) J.L.Morrison and M.A.Dzieciuch, Can.J.Chem. 37(9),1379 (1959)
- 8) S.Brunauer et al., J.Am.Chem.Soc. 60,309 (1938)
- 9) G.M.Dorris and D.G.Gray, JCS, Faraday Trans.I 77,713 (1981)
- 10) A.R.Urquhart and A.M.Williams, J.Text.Inst. 15,T-138 (1924)
- 11) M.F.Froix and R.Nelson, Macromolecules 8(6),726 (1975)
- 12) Y.Ogiwara et al., J.Appl.Polym.Sci. 14,303 (1970)
- 13) H.W.Starkweather Jr., J.Polym.Sci.,B 1(3),133 (1963)



## SUMMARY

The aim of these experiments is to compare the detergency (or the efficiency of soil removal) of several surfactants used in conservation. A non-ionic and an anionic surfactant were chosen as representative of those used by textile conservators and formulated to produce a series of detergents by varying concentrations and the addition of a soil anti-redeposition agent. In this manner the detergent performance with respect to surfactant type, surfactant concentration and anti-redeposition agent concentration is examined. Some assessment of soil deposition in the wash-bath is also made.

SOME EXPERIMENTS COMPARING THE PERFORMANCE OF DETERGENT FORMULATIONS BASED ON ANIONIC AND NON-IONIC SURFACTANTS UNDER CONDITIONS RELATING TO CONSERVATION USE

Nicholas Eastaugh  
Scientific Advisor/Tutor  
The Textile Conservation Centre  
Apartment 22, Hampton Court Palace, East Molesey, Surrey, England

### Introduction

Techniques for the evaluation of soil removal and soil redeposition are well established for commercial products and most of these are readily adapted to the requirements of this study. However, there are two aspects which differ here significantly from other studies. These are the nature of the soiled fabric and the conditions under which the wet cleaning takes place. This paper will deal specifically with developing the detergent formulation examined in these experiments, the nature of the soil test fabrics and the wet cleaning procedure employed, the detailed results of the performance of the various detergent formulations and an assessment of the performances as they relate to detergency theory.

### Detergent Formulation

In this set of experiments it was decided to concentrate on evaluating the efficiency of two surfactants - an anionic (Orvus WA paste) and a non-ionic (Synperonic N). These were to be formulated in different ways to examine the effect of changes in surfactant concentration and the role of the soil anti-redeposition agent sodium carboxymethyl cellulose (CMC). All formulations were to be tested on wool and cotton. Concentrations of surfactant were selected so that there would be significant differences around the normal working concentration, where the 'normal' working concentration was close to the surfactant critical micelle concentration.

Three levels of addition of carboxymethyl cellulose were also investigated, the type of CMC used being Hercules Cellulose Gum 7LXF, a sodium carboxymethyl cellulose of low viscosity (i.e. low m.w., corresponding to a d.p. of about 400) and degree of substitution 0.65 - 0.85. Choice and use of this particular compound has been described in some detail in the conservation literature. Nine different formulations were devised (four with Orvus WA and five with Synperonic N), to allow investigation of concentration and CMC addition. In addition a standard was run using water only (i.e. no detergent addition).

Table 1

1. Water only.
2. 0.025% v/v Orvus WA + 0.005% w/v. CMC.
3. 0.25% v/v Orvus WA + 0.005% w/v. CMC.
4. 0.25% v/v Orvus WA.
5. 0.20% v/v Synperonic N + 0.005% w/v. CMC.
6. 0.20% v/v Synperonic N.
7. 0.50% v/v Orvus WA + 0.005% w/v. CMC.
8. 0.10% v/v Synperonic N + 0.005% w/v. CMC.
9. 0.60% v/v Synperonic N.
10. 0.20% v/v Synperonic N + 0.02% w/v CMC.

The final choice of formulation was on two grounds: firstly to provide suitable experimental material and secondly, to reflect usage within textile conservation. For example, although anionics are generally superior to nonionics in their ability to maintain soil suspension, it appears to be practice to add CMC to Orvus WA paste. Therefore the addition of CMC was investigated.

### Soiled Fabric Samples

The use of standard soil samples for detergency experiments is well established, and the problems associated with how representative such standards are clearly understood.

Obviously the aim (as with any scientific experiment) is to create a reference, eliminating as far as possible unknown variables. Therefore fabrics that are soiled with clearly defined soil components in a reproducible (i.e. controlled) manner must be selected for this type of experiment.

The soil test fabrics used for these experiments were those produced by Testafabrics. These are manufactured by printing the soil on from an engraved roller, and supplied in 10 yard rolls

nine inches wide. The soiled portion is approximately  $3\frac{1}{2}$  inches wide. An extensive range of substrate fibres are available but only cotton and wool used here. The cotton is a bleached sheeting and the wool a chlorinated challis. The soil used is a complex mixture of oils and fats:

1.3%	Keltex (thickener)
2.2%	Corn starch
72.4%	Water
14.0%	Oil (mineral)
.42%	Oleic acid
.36%	Morpholine
1.7%	Vegetable fat (Spry)
.3%	Butanol
4.4%	Solvesso 150
.7%	Ethyl cellulose
.7%	Carbon black
98.4%	(with allowance made for working/mixing loss)

(Data supplied by Westlairs Ltd. 11/8/82.)

#### Wet Cleaning Procedure

It was decided that the wet-cleaning procedures to be employed in these detergent evaluations should, as far as reasonably possible, reflect practice at the Textile Conservation Centre. There were three washbaths and 750ml. of washing solution was used for each bath - a quantity sufficient to cover the samples to a depth of about 1cm. For the cotton this is a bath ratio of about 86:1 and for the wool about 114:1, sufficient in both cases to establish an equilibrium situation where the washbath may freely supply surfactant without significant depletion and remove soil as efficiently as the detergent will allow. For each sample 750ml of washing solution was first of all put into the washing tray and the temperature noted. The sample was then laid onto the water and the rate of wetting out noted. A five minute initial soaking period was allowed.

During the next five minutes 'press and release' sponging was employed followed by a further five minutes soak. The bath water was then poured out and the samples left for a further 10 minutes before the next bath, this was taken to be an average draining time. After the third wash bath cycle, the sample was given a five minute flood rinse and patted with a cupped hand. This procedure was repeated twice.

Following the two flood rinses the sample was drained and left to stand for two minutes. Five rinse baths each of 750ml of softened water and lasting 10 minutes each were then given.

Finally, samples were blotted between folded acid free blotting paper and left to dry naturally. Temperature, pH, colour of bath water and levels of foaming were noted throughout the experiment. All water used was softened.

#### Evaluation of Detergency

Methods for evaluating the detergency achieved can be divided into two groups: those that assess the appearance (either subjectively or instrumentally) before and after washing, and those that determine changes in the soil content through washing. In practice the difference in these approaches amounts to either determining how clean something looks or how much soil has been removed. The former involves either visually grading samples or measuring spectral reflectance and determining chromaticity co-ordinates or some other expression of colour specification, while the latter methods are generally more orientated around quantitative chemical analysis such as gravimetric determinations or the use of radio-tracers.

A choice, therefore, has to be made as to which aspect one is most interested in. For example, in commercial laundry investigations it is going to be the subjective visual evaluation which is of most importance, since any product will be judged on how clean the laundry looks. However, in textile conservation it could easily be argued that we are more concerned with actual soil content after treatment - that is, for the benefit of the object it is the soiling level which is more important than the immediate visual change. It is this line which has been followed in the analysis of these experiments.

Given that we are interested in actual soil contents, then the evaluation method must be instrumental. That is, the method must involve the use of techniques suited to quantitative analysis. Two



have already been mentioned - radiotracers and gravimetric measurements - but neither of these is satisfactory here. The first requires the use of radioactive soils and highly sophisticated instrumentation while the second is difficult to implement on small samples (there is a very high experimental error). Another approach is to use optical analysis through determination of spectral reflectance and rather than convert this into an expression of colour appearance or colour differences, use the reflectance values directly. This will either give figures representing greyness, or else may be used via what is known as Kubelka-Munk theory to determine a quantity related to actual soil content. This last method has found wide application in detergency studies and is the one pursued here.

The reflectance readings were taken on an Instrumental Colour Systems 'Micromatch' spectrophotometer, which is a computer interfaced machine based on a Macbeth 'Colour-Eye' spectrophotometer. This will take simultaneous readings at 16 different wavelengths from 400-700 n.m. (20 n.m. intervals). Tristimulus values were also determined, on an Elrepho (Carl Zeiss) Instrument. The Kubelka-Munk k/s values were computed from 460 n.m. reflectance data using the relationship:

$$k/s = \frac{(1-R)^2}{2R} \quad - (1)$$

where R is the reflectance value. To avoid problems of incomplete hiding of the test fabrics, samples were folded into four for readings.

### Results

Reference should be made when examining the following results to the information on detergent formulation contained in table 1. Samples are labelled 1-10 according to which formulation was used and either C or W depending on fabric type, i.e. cotton or wool. Table 11 contains the basic reflectance data derived from measurements at 460 n.m. This has been converted via the Kubelka-Munk relationship to K/S values (N.B. Fractional, not percentage values of reflectance are used to give K/S).

TABLE II

Sample		R% at 460 n.m.		K/S	
Wool/ Cotton	Number	Soiled area	Unsoiled area	Soiled area	Unsoiled area
C	1	32.2	77.1	0.714	0.0340
C	2	33.8	77.5	0.648	0.0327
C	3	42.5	77.8	0.389	0.0317
C	4	40.8	78.1	0.429	0.0307
C	5	38.5	78.0	0.491	0.0310
C	6	38.9	77.9	0.480	0.0313
C	7	46.4	77.4	0.310	0.0330
C	8	37.0	77.8	0.536	0.0317
C	9	40.6	77.6	0.435	0.0323
C	10	38.9	78.2	0.480	0.0304
W	1	23.9	48.2	1.212	0.278
W	2	27.0	48.8	0.987	0.269
W	3	38.6	50.7	0.488	0.240
W	4	38.7	49.9	0.485	0.252
W	5	31.2	50.3	0.759	0.246
W	6	31.7	50.2	0.736	0.247
W	7	41.7	52.4	0.408	0.216
W	8	31.2	50.9	0.759	0.237
W	9	36.1	52.3	0.566	0.218
W	10	32.5	49.7	0.701	0.255

To use these figures to give us a measure of detergency, we must now take the K/S value and establish what change has taken place during the wet cleaning. To do this we are essentially determining the difference of K/S for the soiled area before and after cleaning. However, it is also necessary to take into account the basic K/S value of the unsoiled area, therefore this will also appear explicitly in our calculations. Finally, it must be noted that this determination of detergency is in fact a relative value, based on the change from some standard. In these calculations the measure of detergency was made with respect to a reference sample cleaned in water alone.

The simplest form of the soil removal equation is given by:

$$\text{Soil Removal (SR) \%} = \frac{\text{Difference in soil level of area}}{\text{Original level of soiling}} \times 100 \quad - (2)$$

Using values of K/S for soiled and unsoiled areas of the reference and cleaned samples, this equation becomes:

$$\% \text{ SR (K/S)} = \frac{(K/S)_s - (K/S)_w}{(K/S)_s - (K/S)_o} \times 100 \quad - (3)$$

Where:

(K/S)<sub>s</sub> is the K/S value for the soiled area of the reference sample.

(K/S)<sub>o</sub> is the K/S value for the unsoiled area of the reference sample.

(K/S)<sub>w</sub> is the K/S value for the soiled area of the washed sample.

However, an advantage of the Kubelka-Munk relationship is that corrections may be applied for extraneous effects such as soil redeposition which may obscure the detergent action we wish to measure. This may be done with fairly good validity by using values of K/S for unsoiled regions of the test fabric for before and after treatment. Equation (3) can then be modified to give 'absolute percent stain removal' as follows:

$$\% \text{ SR}_{\text{abs}} = \frac{((K/S)_s - (K/S)_w) + ((K/S)_a - (K/S)_o)}{(K/S)_s - (K/S)_o} \times 100 \quad - (4)$$

where (K/S)<sub>s</sub>, (K/S)<sub>o</sub> and (K/S)<sub>w</sub> are as above and (K/S)<sub>a</sub> is the (K/S) value for the unsoiled area of the test sample after washing. Equation (4) may be re-arranged to give:

$$\% \text{ SR}_{\text{abs}} = \frac{((K/S)_s - (K/S)_o) - ((K/S)_w - (K/S)_a)}{(K/S)_s - (K/S)_o} \times 100 \quad - (5)$$

Finally, equation (5) can be reduced to:

$$\% \text{ SR}_{\text{abs}} = \left( 1 - \frac{(K/S)_w - (K/S)_a}{(K/S)_s - (K/S)_o} \right) \times 100 \quad - (6)$$

Table III gives values of %SR<sub>abs</sub> based on equation (6) for test samples 2-10, with sample 1 as reference standard.

Table III

SAMPLE	% SR <sub>abs</sub>	
	COTTON	WOOL
2	9.5	23.1
3	47.5	73.4
4	41.4	75.1
5	32.4	45.1
6	34.0	47.6
7	59.3	79.4
8	25.8	44.1
9	40.8	62.7
10	33.9	52.2

#### Removal of soil

Although this is not the place to review the various mechanisms known to operate in detergency (there are a number of excellent discussions, such as those in reference (i)) a brief outline of the processes will serve to introduce the results of this study and their interpretation.

The mechanisms that can operate in the removal of organic soil are these:

1. The 'rolling-up' mechanism.
2. Soap formation.
3. Solubilization.
4. Mesomorphic phase formation.
5. Break up of polycrystalline aggregates.

Each will be characterised by the conditions under which it predominates or contributes to a significant degree to the overall soil removal. For example, soap formation will occur if the soil is saponifiable and the detergent solution hot and alkaline. Hence, it is unlikely to be of importance in conservation wet cleaning. Rolling-up, on the other hand, is a frequently quoted mechanism which has important implications for detergent formulation in that it is most efficient at or near to the critical micelle concentration (confusingly abbreviated as cmc) of the surfactant. However, to be effective it requires a mobile organic soil of relatively low viscosity. There will be many soils that are solid



at room temperature and consequently unremovable by a 'rolling-up' process. In these cases mechanisms 3 and 5 can become important, although the break up of polycrystalline aggregates normally only takes place in significantly alkaline conditions. It is doubtful whether mesomorphic phase formation can play a significant role in soil removal at lower temperatures as the viscosity of the phases will again be high, a fact that mitigates against the process of their formation and dispersal. However, it may be of interest where short chain fatty acids, mono- and diglycerides and sterol esters are present in the soil (which are more readily removed) and when plenty of time is allowed, such as with prolonged soaking.

When interpreting the results in terms of mechanism we shall be looking for the features of the soil removal versus surfactant concentration relationship which indicates what process is predominating. In particular, the surfactant concentration at which maximum soil removal occurs is strongly indicative.

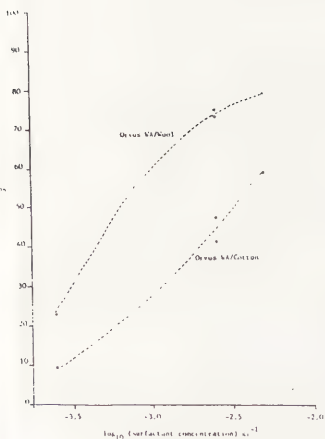
#### Relationship between % soil removal and the detergent formulations.

Any conclusions must begin with an examination of the results contained in table III. From this we will be able to draw more general conclusions about the detergency mechanisms operating under the conditions used.

We are interested in:

- i) The effect of surfactant concentration on detergency.
- ii) The effect of surfactant type on detergency.
- iii) The role of the substrate, i.e. cotton or wool.
- iv) the effect of anti-redeposition agent in relation to its concentration and the nature of the substrate.

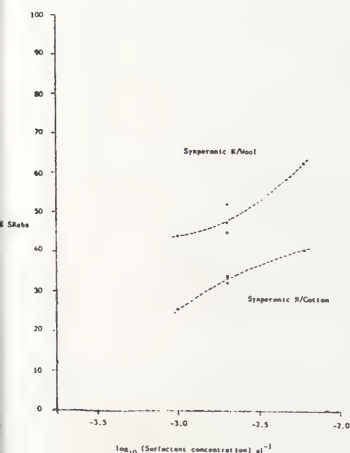
In the following two graphs, all the data available from the experiments has been plotted. However, four sets have been established corresponding to Synperonic N and Orvus WA paste each for cotton and wool. For each set a quadratic regression line has been calculated and plotted.



Before we proceed to any discussion of soil removal mechanism, it is necessary to point out that there is a difference in the surfactant concentration scales for Orvus WA and Synperonic N that relates to molecular weight and the active constitution of the surfactants as supplied.

Molecular weight is easily established; sodium dodecyl sulphate has a M.W. of 288, and a nonyl phenol ethonylate with eight ethylene oxide units has a M.W. of 572 (approximately twice that of the anionic). The significance of this lies, of course, in that it is the molarity (and hence the number of molecules of surfactant available) which will influence detergency rather than weight of surfactant. The difference in active concentration between Orvus WA and Synperonic N is not great: manufacturers' data shows that approximately 28% of Orvus WA as supplied is alkyl sulphate, while 27% of Synperonic N is surfactant. There is also a slight density difference - specific gravity (the density relative to water) is quoted as 1.05 for Orvus WA and 1.02 for Synperonic N. Therefore, the difference in making up solutions as either v/v or w/v only accounts for about 3% error.

Overall then, we can say that there will be a factor of approximately two by which Orvus WA is more active than Synperonic N, but that if we wished to re-label the surfactant concentration axis into moles per litre then it would be necessary to take into account the factors of dilution within the products as supplied. Converting this into log (concentration) there is a difference between scales of 0.3 units (e.g. - 2.2 on the Synperonic N log (concentration) scale corresponds approximately to - 2.5 on the Orvus WA scale) for the molecular weight factor.



Having established the relationship that exists between the two concentration scales as presented so far, it must be further remarked that critical micelle concentration is significantly different for non-ionics and anionics. Non-ionics achieve cmc at a factor of approximately 10 times lower concentration than do anionics. For a dodecyl sulphate the cmc is around  $10^{-2}$  moles/litre, while for a nonylphenol ethoxylate similar to Synperonic N the cmc is around  $10^{-3}$  moles/litre. Therefore, the cmc on our scale is about -2.7 for a non-ionic like Synperonic N and about -2.0 for an ionic like Orvus WA. The cmc for any particular surfactant should, of course, be properly determined by means of a measurement of a property like surface tension value for

accuracy, although the figures just quoted will give some guide. Data supplied by the manufacturers correlates well with the above estimates.

Considering the results for Synperonic N first, it is clear that the % soil removal does not reach a maximum value within the surfactant concentration range examined for either the cotton or wool samples. This is despite the fact that one of the concentrations was three times the (approximate) cmc value. Neither is there any apparent levelling off. From this we might directly conclude that for the experimental conditions there is no advantage to using Synperonic N at its cmc. In fact a higher detergency can be achieved by increasing the surfactant concentration, certainly within the levels tested. Other controlling factors will, of course, apply to limit the degree to which this can be pursued and we might note foaming and soil redeposition as examples. Table IV gives the qualitative descriptions of foaming found during the experiments.

Table IV. Foaming of detergent formulations.

<u>Formulation No.</u>	<u>Foaming</u>
1	None (water)
2	Medium
3	High
4	High to very high
5	High
6	Medium to high
7	High to very high
8	Medium to high
9	Medium
10	Medium to high

In terms of soil removal mechanism we can also suggest that these results are in accordance with the proposition that solubilisation and/or mesomorphic phase formation is operating. This is to be expected from the known behaviour of non-ionic surfactants.

With Orvus WA the situation is different. Some levelling off of the soil removal is apparent at the higher concentrations, particularly for wool. This is despite the fact that the cmc lies beyond the highest concentration tested. Although it is strictly not correct to extrapolate our results, we might suggest that a maximum value is being approached somewhere in the region of the cmc. If this is so, then the optimum concentration, as far as soil removal is concerned, will indeed be around the cmc value. The results for Orvus WA and cotton are less conclusive and more testing is needed to establish soil removal at (and beyond) the cmc.

So far, then, we have established that these tests indicate:

- i) Soil removal increases with increasing surfactant concentration within the range tested.
- ii) The soil removal appears to level off as the surfactant concentration approaches the cmc for the anionic but not for the non-ionic.
- iii) the soil removal mechanism appears to be different for the two surfactant types (a consequence of (ii)).

We may also note that:

- iv) At working concentrations the detergency of Orvus WA on the test samples is higher than Synperonic N for both cotton and wool.
- v) Soil removal is significantly greater for both surfactants on wool than for cotton.

With point (v) it is difficult to ascribe reasons for this, in that it is impossible to evaluate factors associated with sample preparation, i.e. to what extent soil adhesion is dependent on how the soil was applied to the fabric. However, the fact that the difference is so great suggests that the detergency is critically affected by the nature of the substrate. Moreover, the slight differences in the soil removal/surfactant concentration relationships with both surfactants for the two fabrics may also relate to substrate factors. More data would be required to confirm this by establishing the soil removal/surfactant concentration characteristic with greater precision for each case.



The effect of carboxymethyl cellulose

If we were to plot all the results instead of soil removal against surfactant concentration as soil removal against percentage carboxymethyl cellulose in the formulation, then we would not find any clear results. The reason for this is obvious - the effect of surfactant concentration is much more significant than the level of CMC in terms of how much soil is removed. So, rather than display this information in graphical format, the role of CMC in overall soil removal will be presented as a table. By selecting certain of our data, we can compare % SR with % CMC at a constant surfactant concentration - in fact the formulations were carefully chosen so that the surfactant concentration was similar to what might be used in textile wet-cleaning treatments.

Table V

a) 0.2% v/v Synperonic N			
	<u>% CMC</u>	<u>% SR abs. Cotton</u>	<u>% SR abs. Wool</u>
	0.000	34.0	47.6
	0.005	32.4	45.1
	0.2	33.9	52.2
b) 0.25% w/v Orvus WA			
	<u>% CMC</u>	<u>% SR abs. Cotton</u>	<u>% SR abs. Wool</u>
	0.000	41.4	75.1
	0.005	47.5	73.4

Now, although an initial examination of these results might suggest that, for example, Synperonic N performs worst with small additions of cmc, certain extra factors must be taken into account before the final assessment is made. First of all it is necessary to know how significant the differences in % SR abs are - and this means we must know the size of the errors that have occurred. For example, the % SR abs for Synperonic N on cotton at 0% and 0.02% cmc, the difference in soil removal is only 0.1%, which is well within even the accuracy of the reflectance measurements on the sample. Of greater significance is the result for Orvus WA, where there was a 6% improvement in % SR abs for cotton but a small drop in performance for wool. Here we can say that CMC probably enhanced soil removal under the experimental conditions for cotton. The apparent dip in % SR abs for Synperonic N with 0.005% CMC may be significant but would require more data before it is statistically valid.

So far we have been discussing the effect of CMC on the percentage soil removal. We are interested though in what is termed soil redeposition, that is, the effect whereby soil initially removed from the fibre by detergency is redeposited back on the fibre. Unfortunately, the data presented to this point is unsuitable for the purpose (in that it has been evaluated relative to the soil removal of water and small quantity of soil will be removed by water alone and in all probability largely redeposited). What can be examined instead is the soiling of the unsoiled areas of the fabric samples. The Kubelka-Munk relationship can be employed again, with k/s values determined for the samples given in table IV plotted against % CMC.

Table VI

a) 0.2% v/v Synperonic N			
	<u>% CMC</u>	<u>K/S</u>	
		<u>Cotton</u>	<u>Wool</u>
	0.000	0.0313	0.247
	0.005	0.0310	0.246
	0.020	0.0304	0.255
b) 0.25% w/v orvus WA			
	<u>% CMC</u>	<u>K/S</u>	
		<u>Cotton</u>	<u>Wool</u>
	0.000	0.0307	0.252
	0.005	0.0317	0.240

The k/s value is inversely related to reflectance but directly related to soil content, so the higher the k/s the higher the soil level. However, once again we come upon the problem of significance, in that the differences between values is small - in the region of experimental error. Hence we can only be sure of the fact that soil redeposition is small in comparison to detergency or soil removal as a whole. For objects undergoing a single wet cleaning with conditions similar to those of this experiment, we might therefore find a similar outcome: the level of soil rede-

position significantly lower than the effect of differences in surfactant concentration on soil removal.

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#### Bibliography

The following works have been referred to frequently during the preparation of this paper:

- i) Cutler, W.G. and R.C. Davis. Detergency: Theory and Test Methods Pts. I and II. Marcel Ke
- ii) Niven, W.W. Fundamentals of Detergency. Reinhold Publishing Co. (1950).
- iii) Davidsohn, A and B.M. Milwidsky. Syu 6th Edition. George Goodwin Ltd., London. (1978).
- iv) Hofenk de Graaff, J.H. 'The Constitution of detergents in connection with the cleaning of ancient textiles'. Studies in Conservation 13 (1968) pp 122-141.
- v) Smith, A.W. and M.H. Lamb. 'The prevention of soil redeposition in the cleaning of historic textiles'. Preprints ICOM Committee for Conservation 6th Triennial Meeting, Ottawa, 1981.
- vi) Hofenk de Graaff, J.H. 'Some recent developments in the cleaning of ancient textiles'. Preprints IIC Washington Congress, September 1982. pp 93-95.
- vii) McLaren, K. The Colour-Science of Dyres and Pigments. Adam Hilger, Bristol (1983).
- viii) Taylor, R.J. Theory of Detergency. Unilever Education Booklet, Advanced Series, No. 7 (1969).



## SUMMARY

Textile restorers of many museums of history encounter difficulties in the preservation and restoration of the numerous existing single-sheet flags with double-sided painting, many of them centuries old. The most varied conservation methods failed to yield satisfactory results. This is explained, among other things, by the instability and density of the reinforcing tissue. After many experiments, a reversible conservation and restoration method was developed at the Museum of German History, which complies with the present requirements and demands. It constitutes a modified method of known procedures.

# A METHOD OF CONSERVATION AND RESTORATION OF APPLIED SINGLE-SHEET FLAGS WITH DOUBLE-SIDED PAINTING AND EMBROIDERED DOUBLE-SHEET FLAGS

Eva Fischer, Ruth Rothhaar  
Museum of German History  
Unter den Linden 2, Berlin, 1080, GDR

## Starting situation

Museums of history are frequently "plagued" by their voluminous stocks of historic flags and banners. Their condition of preservation may be wanting for various reasons. Among the objects in the worst condition the group of flags made of natural silk is the most conspicuous. The Museum of German History possesses approximately 600 historic flags of this kind. Their date of origin ranges from the beginning of the 18th century to the end of the 19th century. Quite a few of these silk flags are older than 250 years.

Silk of that age as a rule shows no cohesion capacity. Different kinds of environmental influences destroyed the basic molecular structures almost completely. Nevertheless, these fragmentary remnants of historic flags are worth preserving.

The condition prior to restoration in many cases is such, that individual fragments of the flags are only held together by netting. This method of conservation, applied as early as around 1900, up to the Thirties of this century, undoubtedly preserved many flags from complete disintegration, but the detrimental effect of such netting is clearly evident. Among other things, it rubs against the brittle, worn silk, causing further damage. Protection against dust and climatic influences is by no means assured in this way, and the method does not ultimately serve the main purpose of stabilising the brittle silk.

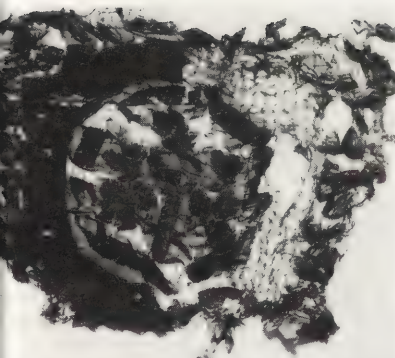
If the procedure is started by separating the netting from these extremely unstable silk flags, conservation and restoration measures must follow without delay. There is no way back; restoration only with thread and needle and without the reinforcement with firm tissue is not possible. Apart from the fact that the thread would not find any hold, each needle-stitch would only worsen the damage. Nor does the customary method of embedding in crepeline solve the problems, since the brittle silk, i.e. the flag fragments, would not find any hold in the crepeline. The solution of using firm reinforcement tissue will only cause a reduction by 50 per cent of the specific character of single-sheet flags with double-sided painting. Flags with the same designs on both sides may still be treated in this way. This also appears recommendable under certain aspects of conservation. Functions of reinforcement and protection both become effective by this method. The latter is particularly suitable for flags to be shown in a permanent exhibition. Naturally the 50 per cent reduction of original design needs to be taken into consideration.

For flags kept for their documentary significance, occasionally exhibited for shorter periods the covering of one side for purposes of reinforcement proved unfavourable. A method had to be found which would preserve the original character, at the same time ensuring the conservation of the object.

We therefore came back to the method of embedding in two layers of crepeline.

## Experiments

Complicated problems arose in the process of embedding flags within two layers of crepeline, caused by material and size. Comparatively large flags with painted or applied designs often have an unduly great net weight, incompatible with the stability of the reinforcing silk tissue. Crepeline is a light tissue which does not stand up to any great load. It turned out in the course of restoration work, that crepeline alone could not sufficiently reinforce the flag. Conservation work also proved to be difficult. In the course of sewing work the thread slid away, the tissue lost shape and the whole surface remained limp. Ways had to be found to reinforce the crepeline and to prevent it from sliding away. We saw one variant in the application of polyacrylates. We were aware that this would give rise to reservations, if not objections among experts. The indiscriminate application of reinforcement methods by means of synthetic re-



before the restoration in the net



before the restoration after removal of the net



sins caused a great deal of partly irreparable damage in the past. A method therefore had to be found to use the advantages of polyacrylates and to avoid causing damage. Our procedure makes this possible. Polyacrylate remains in the reinforcing layers of crepeline tissue without penetrating the original textile fabric. The advantages of this synthetic resin are used without adhesion.

Nevertheless, even we still have doubts and reservations in regard to this method of stabilising crepeline. These in the main relate to the following problems:

- the electrostatic behaviour of polyacrylates attracting more dust particles, with the consequence of a shabby, dirty appearance of the object;
- the shining surface of the polyacrylate negatively influences the aesthetic general impression;
- the question arises, whether the application of some synthetic fabric would not be less problematic than the additional stabilisation of crepeline with synthetic resin.

A series of systematic experiments was conducted at the Museum of German History, with the participation of students of the College of Restoration, specialising in textile conservation, in order to investigate these substantiated objections.

The arrangement of this experimental series corresponded to the aspects listed above.

#### 1. Application of a non-electrostatic agent to stabilise the crepeline.

We tried to stabilise the crepeline by means of non-adhesive agents of an assortment offered for sale in the shops. The most suitable substance was found to be "Neoprint", a binder used in the printing industry. Its most outstanding physical and chemical properties are: colourless, not electrostatic, soluble in water in any ratio, pH-value 7. The experiments, conducted in different variants, both as regards consistency and arrangement, all had negative results. The difference between treated and untreated crepeline was too negligible; the reinforced material inadequately complied with our demands.

#### 2. Application of polyacrylates in varying concentrations.

We came back to the reinforcement of crepeline with polyacrylate and we tried to reduce the properties of this synthetic resin which were negative for purposes of conservation and restoration. A concentration of polyacrylate had to be found, in which the properties positive for our purpose, i.e. the stabilisation of crepeline, were still effective. The disadvantages - the shining and electrostatic effects - were to be reduced.

For these experiments we used a dispersion of a polyacrylic acid ester with the trade mark Polyacrylate D 320, produced by the VEB Chemische Werke Buna in Schkopau, with the trade mark Polyacryl D 320. A new product of this kind is now on the market with the trade mark Schkoakryl PAA. It is a synthetic resin soluble in water, which remains flexible after solidification and adheres in complete transparency to the carrier material. Temperature and pressure can activate the adhesive power. This synthetic resin is applied in many other areas of restoration. It should be recalled, that it has been used for years in the conservation of textile material objects dating back to prehistoric and early historic times.

For our purposes the important point is to find the right concentration. The experiments were related to the proportions of polyacrylate and water in the solution applied, of 1:6, 1:7, 1:8, 1:9, 1:10. The tests revealed that the proportion of 1 part of polyacrylate to 8 parts of water yielded the best results.

The adhesive effect was very slight, the disturbing shine had been excluded, almost entirely, and yet the stability to reinforce the crepeline was preserved. Its further application in the process of conservation was assured. Thanks to the minimum distribution of the polyacrylate dispersion over the surface of the reinforcing tissue, there were no obstacles in the way of the reversibility of the subsequent phases of work. In the rare cases in which carrier material is separated from the original, no limitations are imposed. The possible adhesion of dust



Preparation to the cleaning in gauze



particles is hardly greater than in untreated crepeline thanks to the low binding properties. Dirt can be removed by washing the entire embedded object, even in cold water. No modifications take place. Several samples were tested also to this effect.

### 3. The use of synthetic material for embedding

For this series of experiments the synthetic polyester material "Stabiltex" was used. We applied it in a linen fabric, as in catalogue no. 4.

Work with this material was by far more complicated than with unreinforced crepeline. Its thread is stiff and bristled compared with that of natural material. At the same time the synthetic tissue is very smooth and tends with preference to shift into a diagonal position. Turning over and hemming in the edge was unsatisfactory, despite repeated fastening. This is of a disadvantage to the appearance of the object and looks untidy in finish. Nor could thermal treatment, e.g. by ironing, yield the desired effect. Apart from the purely technical difficulties with the synthetic crepeline substitute during restoration, further disadvantages became evident. Thus, "Stabiltex" cannot be dyed. Although sold in different colour shades, it cannot in every case be obtained in the respective required colours close to those of the object under restoration. The range of colours offered is not sufficient.

Moreover, "Stabiltex", with thicker fibre and greater density, is not as transparent as crepeline. It therefore lies over the original very conspicuously and disturbingly. The mentioned technical difficulties and the aesthetic disadvantages induced us to return to the use of crepeline.

The above described experimental series opened the way to finding positive answers to the questions raised at the beginning and for complying with all demands. Crepeline can be effectively stabilised, at the same time leaving the conservation process reversible. The necessary subsequent work operations in conservation and restoration are exclusively needle-work. Original parts are stitched up in the traditional way.

### Conservation and restoration with reinforced crepeline

Every treatment is preceded by a thorough investigation of all available materials. In most cases this is followed by cleaning. For this process as well the preceding analytical investigation was an important prerequisite. If the colours are water-resistant, damp cleaning is possible. Good results were obtained by the following method: the object is slightly smoothed with distilled water, embedded in gauze and then washed in a soap solution (radex saponaria).

The crepeline is carefully prepared. At first it is dyed and then treated with polyacrylate (concentration 1:8). The crepeline is clamped with straight fibres into a frame. The polyacrylate dispersion is applied evenly with a soft brush. After drying, the original material is fixed on with fibres in correct position (mostly only in fragments of 1 cm<sup>2</sup>). A second reinforced crepeline layer serves as covering tissue and is placed with care over the original. The flag now lies flat on the table, embedded between two crepeline layers. At this stage the traditional restoration work sets in.

A round needle and a fine crepeline thread, also dyed, are used for sewing. The condition of the flag determines the sewing technique. If the object is very threadbare and only fragments of the original still exist, the material should not be pierced. This would cause further damage. The stitches have to be taken around the original. Another advantage is derived from the reinforcement of the crepeline with polyacrylate. The warmth of the sewing hands and the slight pressure in the course of work activates the adhesive power of the polyacrylate. The slight adhesion of the layers to one another prevents the fragments from slipping out of position and facilitates the work. This allows a greater economy of stitches. At the same time the slight adhesive effect in no way obstructs the separation of all layers from one another, if this should become necessary.

Good results are not only achieved in the application of polyacrylate reinforced crepeline in the treatment of single-sheet flags. The same may be said of the restoration of double-sheet flags with embroidery, especially metal embroidery. The silk in this case was the grounding of the embroidery. In many ob-



After the restoration



Embroidered double-sheet flag; smallest fragments of silk are held; after the restoration





Detail

jects non-embroidered parts of the silk have completely disintegrated. In those cases only the reinforcing linen tissue is left intact. With the aid of the polyacrylate-reinforced crepe-line, the same procedure as with single-sheet flags may be applied after separation of the two flag sheets.

The flexibility will be retained, since crepe-line is not applied in these places. The stitches are placed alongside the embroidery. The application of this mode of procedure is not even impeded by heavy metal embroideries. The renewed stability of the object allowed the display of restored objects at exhibitions.

#### Concluding remarks

Undoubtedly there may be reservations even in regard to this method. But is that not so with every procedure? Every interference will be a risk. Yet, faced with the task of restoring badly damaged silk objects for purposes of museum documentation, there is no better variant available at present. There is only the choice between two alternatives: to abstain from restoring the object and thereby excluding it from further use - which would mean that it would be completely destroyed in the near future; or application of the procedure elucidated above.

The experiences described are based on the results of investigations and work accomplished in the past four years. According to our opinion the presented method of conservation and restoration of painted single-sheet and embroidered double-sheet flags constitutes the least detrimental procedure for the object in question. At the same time it complies with one of the most important requirements of restorers: it is reversible.



## SUMMARY

The spectrophotometric method allows one to identify in the extracts from dyed fibres most of the red and violet natural dyes and to distinguish them from synthetic ones. A system of extractants is proposed, making it possible to simplify and speed up the analysis of dyes in the microsamples of museum and archaeological textiles. The principal procedures of analysis - scission of the bonds between the dye and the fibre, extraction of the freed dye, and its spectrophotometric determination in the extract - are consecutively performed in the same extractant within 10-20 min. The absorption spectra are given for the main red and violet natural dyes in some of these extractants. Also presented are the results of the spectrophotometric study of dyes in museum and archaeological textiles after their extraction with the help of the extractants proposed.

## SPECTROPHOTOMETRIC DETERMINATION OF RED AND VIOLET NATURAL DYES IN MUSEUM TEXTILES

V.P. Golikov  
All-Union Research Institute of Restoration (VNIIR)  
Krestyanskaya pl., 10  
Moscow 109172  
USSR

Red and violet natural dyes were used in the textiles created before the middle of the XIX c. In analyzing these dyes it is necessary to distinguish them from synthetic dyes of similar colour, as well as to determine individually about 15 natural dyes or their mixtures /1/.

Inasmuch as dyes manifest intensive selective absorption in the visible and ultraviolet regions the spectrophotometric method is effective for their analysis. Two techniques can be applied to determine dyes with the help of this method: directly in the dyed fibres, by the reflection spectra, or in the extracts from dyed fibres, by the absorption spectra. The first procedure is simpler, but requires rather large samples and is unsuitable for soiled archaeological textile. The second technique is considerably more sensitive (only several threads are needed for the dyes to be identified) and applicable to archaeological textile, if one succeeds in isolating the dyes selectively. In the present communication the second technique is considered.

The qualitative analysis of dyes is performed by examining a set of maximums in their absorption spectra. It is also expedient to record the spectra of the derivatives of dyes: their phenolate-anions (when alkalis are added); complex compounds with cations of various metals - Al, Ca, Mg, Cu, Fe, Pb; cations resulting from the protonation of carbonyl groups at highly acid pH, e.g. in  $H_2SO_4$ .

The sensitivity of the method depends on the content of dye in the fibres, its molar extinction, and the width of the maximums in absorption spectra. An important advantage of the method is the simplicity of quantitative analysis, since the intensity of the maximums (or their area) is directly proportional to the concentration of the dyes.

The analysis of dyes in the extracts by means of the spectrophotometric method, as in the case of any other method, includes 3 principal consecutive procedures: 1. scission of the bond between the dye and the fibre; 2. extraction of the freed dye into the solution; 3. spectrophotometry of the dye and its derivatives in the extract.

Each one of these procedures requires specific reagents and its own optimum conditions. The present work was aimed at finding such extractants that would allow performing all the above three procedures without transferring the sample into other reagents. For this to be possible the extractants must effectively sever the bonds with the fibre in direct, vat and, especially, mordant dyes, they must readily dissolve these dyes and their above-mentioned derivatives, and must not possess any self-absorption in the region of the diagnostic maximums of dyes.

The following extractants were used to isolate red and violet natural dyes and determine them spectrophotometrically.

1) Ethanol. Very nearly all the previous synthetic dyes are almost completely extracted from the fibres after 20-30 min at 20°C (or 5-10 min when heated to the boiling point). Mordant natural dyes are not extracted by ethanol. However, direct (carthamin) and vat (indigo) natural dyes can be partially extracted in boiling ethanol.

2) Ethanol + complexone aqueous solution. Any complexone with a high stability constant, e.g. EDTA (Trilon B), can be used for this purpose. 5 drops of 1-5% complexone aqueous solution are added to 5 ml of ethanol, and the dyed fibres are heated during 10-20 min at the boiling point of the mixture. In the presence of water the complexone disrupts the bonds with the fibre in all mordant natural dyes, and ethanol effectively extracts them. This extractant is transparent in the visible and ultraviolet regions, and so it can be used not only for the red and violet but also for yellow, brown and black natural dyes having their principal absorption maximums in the ultraviolet and the short-



wave visible regions.

This extractant is especially suitable for analyzing red sandalwood and dragon's blood, these dyes having the most resolved absorption spectra structure in ethanol. The shortcoming of this extractant is that the presence of water deteriorates the resolution of the maximums in the absorption spectra of the other red and violet natural dyes, caused by the intermolecular interactions of the dye with the water.

3) Dimethyl formamide (DMF). It selectively isolates synthetic dyes and completely extracts all the direct (carthamin) and indigoid (indigo and antique purple) natural dyes from the fibres. In fibres of gray, violet and green colour produced by two dyes - vat indigo and the corresponding mordant dye - first indigo can be selectively isolated with the help of DMF and then - the mordant dyes, using other extractants. Because of DMF self-absorption in the ultraviolet region the absorption spectra of dyes in it can only be recorded in the region of 350-800 nm ( $32-12.5 \times 10^5 \text{ cm}^{-1}$ ).

4) Dimethyl formamide + complexone aqueous solution. The amount of complexone added to DMF is the same as in No. 2 (see above). When heated this extractant, similarly to No. 2, isolates all red and violet natural dyes, including the mordant ones. The advantages of this extractant over extractant No. 2 are its higher recovery rate (5-10 min), as well as the absence of the negative effect of water on the resolution of the absorption spectra fine structure. The latter property is caused by the high-polarity DMF disrupting the hydrogen bonds of the dye with the water, as a result of which many of the red and violet natural dyes yield, even in the presence of water, well-resolved spectra (see Fig. 1).

This extractant is most effective for the analysis of orcein, hematein, brazilein, alizarin (see Fig. 1). The extractant also makes possible selective isolation of red and violet natural dyes from archaeological textiles, because the main contaminants from the soil - humates - are insoluble in it.

5) Concentrated  $\text{H}_2\text{SO}_4$ . Within 5-10 min sulphuric acid dissolves all the dye in the microsample together with the fibre biopolymers. Having no maximums in the diagnostic 400-800 nm region, most important for the identification of dyes, biopolymers do not interfere in determining them. In sulphuric acid all natural dyes yield intensively coloured products stable over a period of 30-60 min. This extractant is most effective, however, in the analysis of dyes producing well-resolved absorption spectra in it: carminic (kermetic) acid, lac-dye, purpurin (pseudopurpurin), alkanin (shikonin), orcein, antique purple (see Fig. 1).

$\text{H}_2\text{SO}_4$  is also suitable for the identification of these dyes in archaeological textile because contaminants from the soil have no absorption maximums in the diagnostic 400-800 nm region. In this region they display a rather intensive continuous absorption, against whose background one can determine the absorption maximums of the dyes.

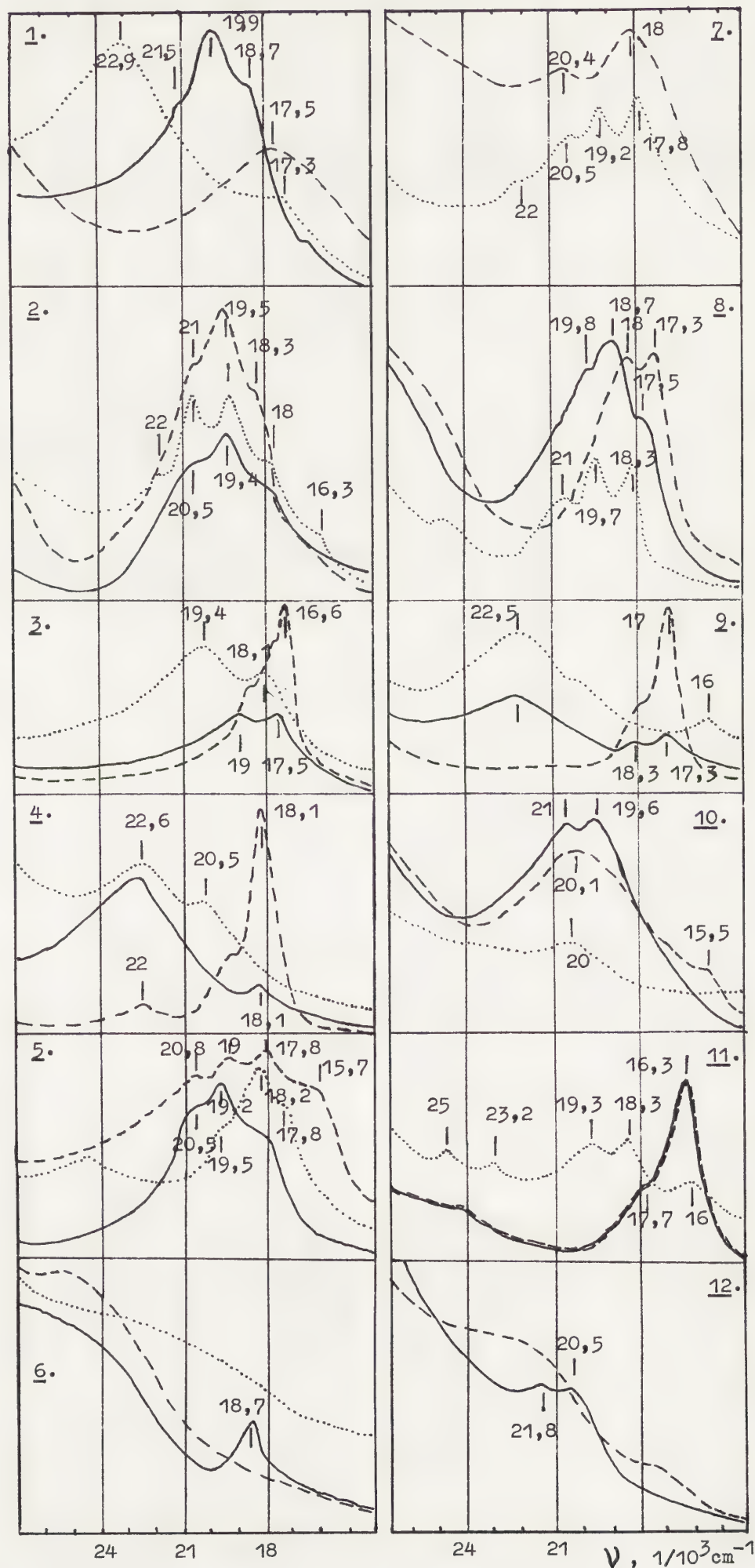
Thus, as seen from Fig. 1, by the absorption spectra in the 350-800 nm ( $30-12.5 \times 10^5 \text{ cm}^{-1}$ ) region one can determine most of the red and violet natural dyes and distinguish them from synthetic dyes. Unfortunately, by means of the spectrophotometric method it is neither possible to distinguish between the alkanin and the shikonin optical isomers, nor between the dyes with similar chromophore systems: carminic and kermesic acids, purpurin and pseudopurpurin /1/.

In the extracts of microsamples, obtained with the help of the extractants described above, a spectrophotometric study of dyes has been performed in I-XIV cc. archaeological textiles, XVII c. sewn icons from the Moscow Kremlin museums, XVII-XIX cc. decorative fabrics from palaces-museums in the USSR.

In the archaeological textiles were identified: antique purple, indigo, as well as kermes, madder and safflower dyes. The analysis of a remarkably well-preserved dark red silk dress of a I c. doll from Siberia showed that the silk had been dyed with practically pure purpurin (or pseudopurpurin). This made it possible to assume that Far Eastern species of *Rubia* (*R. cordifolia*, *R. chinensis*), containing large quantities of purpurin and little alizarin, were used for the dyeing of silks.

In many samples of decorative fabrics, assigned by the museum staff to the XVIII c., synthetic dyes were revealed, which sho-





wed these fabrics to be copies or reproductions of the late XIX-early XX cc. The synthetic dyes in this textile are very similar in colour to the most expensive natural dyes. And, on the contrary, numerous decorative fabrics of the XVIII c. in which natural dyes with a low light stability, e.g. orcein, mahogany brazilein, carthamin, had been used were often regarded by the museum staff as later copies, on the grounds that the dyes in these fabrics had faded greatly.

A surprising fact was that, in all the studied XVII-XIX cc. samples, madder dyes were completely absent. In all the cases when by their colour the fibres appeared to have been dyed with madder, the analysis revealed only orcein or brazilein, often toned with tannins.

Violet colorations in the studied XVII-XIX cc. fabrics were obtained with the help of orcein, sometimes toned with indigo. Orcein, in combination with blue indigo, was also widely used to obtain gray and gray - light blue fibres. In some sewn icons of the XVII c. the violet fibres were obtained using carminic acid and indigo. Very often XVII-XIX cc. fabrics contained 3-4 dyes, needed to obtain the required hue.

Very interesting data were produced by the analysis of dyes from blue flowers in an early XVIII c. fabric with a design of flowers in the "Chinoisery" style. These flowers are woven, according to a purely pictorial principle, out of four gradations of blue, differing in intensity. In the shades the fibres proved to be dyed not only with blue indigo, as in the other 3 gradations, but also with orcein. This made the colour of the shade warmer than the other 3 colours in the flower. Analysis of the dyes thus gives reason to suppose that the impressionist principle of a colour hue changing in the shade was known to the creators of this fabric.

#### Reference

1. Hofenk de Graaf I.H. Natural dyestuffs for textile materials. Origin. Chemical constitution. Identification. ICOM. - Amsterdam, 1969.



## SUMMARY

Herein there was conducted a complex experimental investigation of the immediate effect of cleaning compositions, based on water, ethanol and perchloroethylene, on the fibres and dyes of museum textiles. A microscopic technique was employed to measure a single and repeated deformation of the shape of microfibrils of silk and wool, their diameter and also a change of double refraction in silk. The number of breaks of peptide bonds in silk was evaluated by means of an acid histochemical dye. A spectrophotometric technique was used to study the extraction of red natural dyes of carmine acid and orcein from silk. Water and compositions, based on it, as well as the mixture "ethanol: H<sub>2</sub>O" cause deformation of microfibrils of silk and wool, irreversible changes in the regular microstructure and breaks of peptide bonds in silk fibroin, as well as the extraction of red natural dyes of carmine acid and orcein from silk. A negative effect of these compositions increases as the age of the textile grows, after repeated wetting and drying, as well as for textiles containing different types of fibres. Tetrachloroethylene and compositions, based on it, have a far less effect on the fibres and dyes of museum textiles than compositions, based on water.

Microfibre

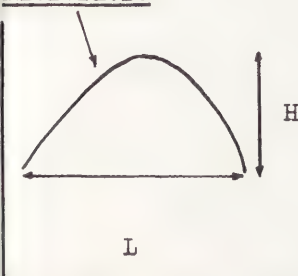


Fig. 1

## COMPLEX EXPERIMENTAL INVESTIGATION OF THE EFFECT OF CLEANING COMPOSITIONS ON THE FIBRES AND DYES OF MUSEUM TEXTILES

V.P.Golikov, S.V.Ustinov  
All-Union Research Institute of Restoration (VNIIR)  
Krestyanskaya pl., 10  
Moscow 109172  
USSR

The cleaning of dirt is the most important and crucial stage in the restoration of museum textiles. Unfortunately, it is difficult at present for restorers to select objectively the safest and, simultaneously, effective cleaning composition, as experimental works on the evaluation of the effect of different compositions on the fibres and dyes of museum textiles practically do not exist. This is, in our opinion, primarily due to objective difficulties of obtaining physico-chemical characteristics of museum textiles by classical methods.

This work attempts to employ a complex of techniques enabling a study of the effect of cleaning compositions on microsamples of museum textiles to be made. A study was made of the effect of twenty-five compositions, based on water, ethanol and tetrachloroethylene CCl<sub>2</sub>=CCl<sub>2</sub> (TCE), on various types of museum textiles: silk and wool fibres of the 17th century tapestry from the "Kuskovo" Palace; on fibres and natural dyes the 18th century decorative silk fabrics from Paul the First's Palace in Pavlovsk; on silk fibres of the 1st century archeological textiles. Contemporary silk and wool fibres were investigated for comparison.

A microscopic investigation of deformation of microfibrils. Individual filaments (microfibrils) in the form of a spiral were extracted from spun silk and wool threads of the 18th century tapestry. They were cut under a microscope into 1-3 mm. long pieces in the shape of an arc (Fig. 1). This shape is convenient for the evaluation of deformation of Microfibrils on a glass plate were placed on the slide of a passing light microscope with whose aid they could be photographed and the parameters "H" and "L" (Fig. 1) of a microfibre arc measured in the original state, five minutes after adding the composition and after its drying. Deformation of 6-8 microfibrils was measured for each composition.

The greatest, and in most cases, irreversible deformation of drying microfibrils of the 17th century silk and wool is caused by a single action of the composition, based on water and ethanol (Fig. 2, Table 1). Deformation of silk and wool microfibrils has in many cases an opposite sign (Table 1), which is particularly dangerous for textiles containing both types of fibres.

Table 1. Alteration in the height (H) and length of the projection (L) of the arc of wool and silk microfibrils from the 17th century tapestry under the effect of cleaning compositions (see fig. 1).

Cleaning compositions	Wool				Silk				
	:After 5 min. : wetting		: After : drying up :		:After 5 min. : wetting		: After : drying up :		
	: ΔH :	: ΔL :	: ΔH :	: ΔL :	: ΔH :	: ΔL :	: ΔH :	: ΔL :	
	1	2	3	4	5	6	7	8	9
Distilled water	+20	-38	+10	-16		+12	-13	+14	-11
"Children's" soap in water	+22	-56	+10	-45		+8	-21	+6	-18
Soap root in water	+9	-18	+8	-18		+8	-20	+6	-17
Ethanol:glyce- rine:water (45:1:55)	+32	-55	+36	-52		+4	0	+3	+10
Ethanol:glyce- rine:water (22:1:78)	+36	-54	+37	-54		-3	+15	-2	+36
Tetrachloro- ethylene	0	0	0	0		0	+10	+2	+2

1	:	2	:	3	:	4	:	5	:	6	:	7	:	8	:	9
Tetrachloro- ethylene + 0.5% of syntanol		-2		0		-3		0		0		+1		0		0
Tetrachloro- ethylene + 0.002% of the mixture "etha- nol:glycerine: water" (45:1:55)		0		0		0		0		-1		+1		-1		+1

$\Delta H = H_K - H_0 / H_0 \times 100\%$ ;  $\Delta L = L_K - L_0 / L_0 \times 100\%$ , where  $H_0$  and  $H_K$  are the height of the arc before and after treatment  $L_0$  and  $L_K$  are the length of the arc projection before and after treatment.

Ionogenic detergents of the "children's" soap, as a rule, increase, and non-ionogenic detergents (syntanol and saponins of soap root) decrease deformation of microfibrils as compared to clean water (Table 1).

Deformation of the 17th century microfibrils after a repeated action of compositions, based on TCE, is slight, or completely absent (Fig. 2, Table 1).

Without treatment

After 5 min. wetting

After drying up

Saturated water solution of the "children's" soap



Mixture "ethanol: glycerine: water" (45:1:55)



Tetrachloroethylene + 0.007% of the mixture  
"ethanol: glycerine: water" (45:1:55)



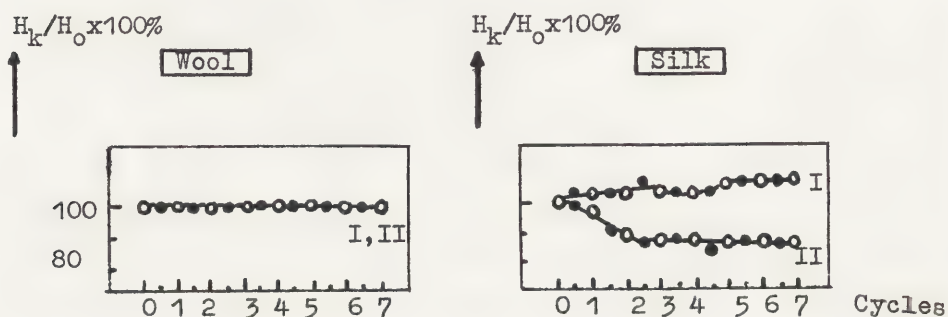
Fig. 2. Microphotographs of the deformation of wool (A) and silk (B) microfibrils from the 17th century tapestry under the effect of cleaning compositions.



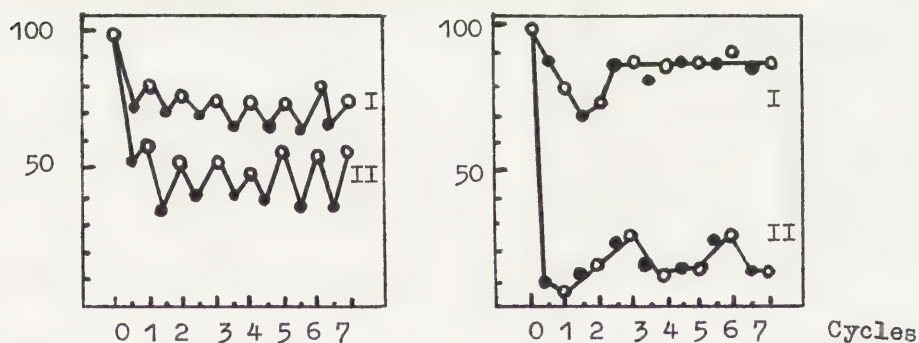
A repeated local cleaning is frequently resorted to in the restoration practice with the aim of "mitigating" the adverse effect of the composition; to do so, an individual area is rubbed with a piece of cotton wool wetted in the composition, dried and then wetted again, etc. In order to evaluate the effect of this cleaning method we measured the deformation of microfibrils after seven cycles of wetting in compositions and subsequent drying. Such a deformation was studied for compositions, based on the three solvents, in the silk and wool microfibrils of the 17th century tapestry and of contemporary textiles (Fig. 3).

The deformation of microfibrils after a repeated action of a liquid composition is in itself a negative factor. However, the appearance of deformation shows that a microfibre is "live" and capable of reacting to the action of liquid agents. The loss of capability of deforming is a sign of irreversible changes.

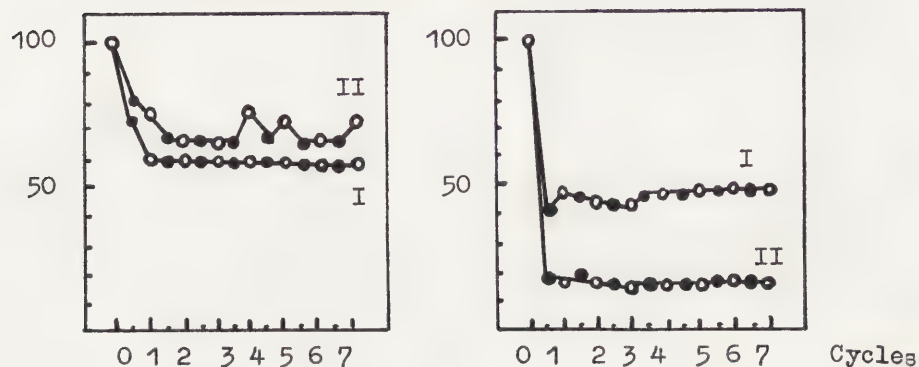
As can be seen from Fig. 3, the composition, based on TCE, has a minor effect on wool microfibrils. Fibres of contemporary and old silk deform slowly to a small extent under the effect of



Tetrachloroethylene + 0.5% of syntanol + 0.002% of the mixture "ethanol: glycerine: water" (45:1:55)



Ethanol: glycerine: water (45:1:55)



The "children's" soap in water

Fig. 3. Alteration in the height of the arc of the microfibre  $H_k/H_0 \times 100\%$  ( $H_k$  and  $H_0$  are the height of the arc after and before the treatment) of silk and wool from the 17th century tapestry (I) and contemporary textiles (II) under the effect of successive cycles of wetting (•) and drying (◦) in cleaning compositions.



this composition. Under the effect of a water solution of the "children's" soap, old wool, as well as old and new silk lose a capability of reversible deformation after repeated wetting and drying, whereas contemporary wool retains such a capability.

A water-ethanol mixture, after a repeated action, causes old silk to lose a capability of reversible deformation.

Minor mechanical efforts by the restorer are sufficient to cause great damage to old textiles after a repeated action of compositions, creating an irreversible deformation of microfibrils.

The evaluation of alterations in the structure of silk microfibrils with the help of a polarizing microscope. Fibroin molecules in silk native microfibrils are oriented parallel to one another, forming a regular structure. Such microfibrils have double refraction and, in a polarizing microscope, they have an interference colouring of the first and second orders, bright and uniform in length. Effects, breaking the regular structure of fibroin, will change the diameter of a microfibril and decrease the order of interference colouring at the expense of decreasing double refraction: bright dark blue, red and green colouring of native fibres will transform into weak yellow or grey. If breaks of the structure are uneven in the fibre length, changes of the colour of interference colouring will also be uneven in the microfibril length.

A study was made of changes in the structure of silk microfibrils from the 17th century tapestry under the effect of the three basic compositions. The diameter of microfibrils increases irreversibly, the amount of double refraction decreases, and interference colouring becomes uneven in the microfibril length in the water solution of the "children's" soap.

The composition "ethanol: water: glycerine" (45:55:1) does not change substantially the fibre diameter and has a slight effect on double refraction, but makes the interference colouring uneven in the fibre length.

Pure TCE causes a uniform swelling of microfibrils, followed by a decrease in double refraction and an increase in the microfibril diameter. But these changes are reversible, as the fibre structure is restored after TCE has dried up.

The evaluation of the number of breaks of peptide bonds in silk fibroin with the help of the bromophenol blue acid dye (BPP). If peptide bonds are broken in fibroin molecules, free  $\text{NH}_2$ - and  $\text{COOH}$ - groups are formed. Basic  $\text{NH}_2$ - groups can be found by dyeing silk with the BPP acid dye. As this dye is a pH indicator (it is yellow with acid pH), the presence of the free acid  $\text{COOH}$ -group, alongside  $\text{NH}_2$ , can be detected by a change in the BPP colouring.

The 18th century white silk and contemporary silk were subjected to the effect of two and ten successive cycles of wetting in TCE, the "children's" soap water solution (I) and the mixture "ethanol: water: glycerine" = 45:55:1 (II) and subsequent drying. After that, the sample was washed for 0.5 min. in clean water and dyed for 3 min. in a 0.1% BPP water solution.

As should have been expected, contemporary silk practically cannot be dyed without the effect of compositions, whereas the 18th century silk is dyed in a blue colour. This means that there are already breaks in the fibroin of the 18th century silk, whereas they do not exist in contemporary silk.

Breaks appear even in contemporary silk under the effect of (I) after ten cycles.

The intensity of the blue colouring of the 18th century silk increases under the effect of (I) and (II) after two cycles. After ten cycles, the blue colouring changes into yellow, which shows, in our view, the acidification of BPP, bound with fibroin, by  $\text{COOH}$ - groups appearing, like  $\text{NH}_2$ - groups, when peptide bonds are broken.

Breaks in the peptide bonds of fibroin do not appear under the effect of TCE, as contemporary silk, even after ten cycles of treatment with TCE, cannot be dyed with BPP, and the intensity of the colouring of the 18th century silk does not change.

The analysis of structural changes in archeological silk by means of scanning electron microscopy. The 1st century archeological silk was treated with water and water solutions of soap, wa-



Fig. 3: Electron scanning microphotographs of the 1st century archeological silk, treated with water solution of "children's soap" (300 $\times$ ). (A) - before, (B) - after treatment.



ter softeners and other agents. Silk microfibres in water solutions swell greatly, dissolve partially and are glued together within one thread. Information on the structural damage to the original and treated silk, obtained by means electron microscopy, is correlated with the results of investigations in polarized light (Fig. 3).

The investigations of the extraction of carmine acid and orcein by the spectrophotometric technique. Microsamples of the 18th century red silk (7x5 mm.), dyed with cochineal and orcein, were immersed in 2 ml. of the composition for 24 hours. After that, 3 ml. of a 1% alcohol solution of 11 NaOH were added to the dye extract in order to preclude the effect of the solvent and pH on the absorption spectra of extracted dyes.

As can be seen from Table 2, dyes are extracted from silk most intensively by the "children's" soap solution and the mixture "ethanol: water" (45:55). TCE and compositions, based on it, are much safer for these dyes in the 18th century silk.

Table 2. Isolation of red natural dyes from samples of the 18th century silk under the effect of cleaning compositions.

Cleaning compositions	Amounts of extracted dyes *	
	Carmine acid	Orsein
Distilled water	1	1
"Children's" soap in water	2.7	3.6
Soap root in water	0.6	1.0
Ethanol: glycerine: water (45:1:55)	1	3.0
Ethanol: glycerine: water (22:1:78)	0.7	1.0
Tetrachloroethylene	0	0
Tetrachloroethylene + 0.002% mixture ethanol: glycerine: water (45:1:55)	0	0
Tetrachloroethylene + 0.1% of water	0	0
Tetrachloroethylene + 0.5% of syntanol	0	0

\* - The concentration of dyes, isolated in distilled water, is equal to unity.

Techniques, employed in this work, can be used for an objective evaluation of the effect of liquid compositions on any part of museums textiles and for the correct choice of the safest compositions. Most of these techniques are easily available in restoration institutions.





## SUMMARY

The cleaning of museum fabrics is one of the most important and critical stages in the process of restoring museum textile materials. The present work was aimed at studying the influence exerted by organic solvent - tetrachloroethylene - on museum textiles, from the point of view of their future prolonged storage. The residual quantity of solvent remaining on the textile fabric after the cleaning was determined by the mass-spectrometric method. Direct control of the polymeric material destruction, after its treatment with tetrachloroethylene and accelerated ageing, was accomplished by means of IR - MATR (multiple attenuated total reflection) spectrometry. Since it is difficult to estimate all the effects that had taken place prior to the exhibit restoration, the method of comparison with the changes in similar modern fabrics was used.

## THE INFLUENCE OF SOME RESTORATION PROCESSES ON MUSEUM TEXTILE MATERIALS

T.N.Gromina  
All-Union Research Institute of Restoration (VNIIR)  
Krestyanskaya pl., 10  
Moscow 109172  
USSR

Museum textiles are mostly represented by woven or knitted cloths and finished articles made of natural fibres of vegetable or animal origin: cotton, bast fibres (flax, hemp. etc.), wool and natural silk.

The cleaning of museum textiles is a complicated and critical stage in the process of their restoration. A number of dirt removal methods are known, of which the principal ones are: cleaning in aqueous medium and in organic solvents ("dry cleaning"). A particular method of cleaning is not infrequently chosen at random because of the absence of studies aimed at determining the influence of organic solvents on museum fabrics, with their future prolonged storage taken into account.

Organic solvents are widely used in everyday dry cleaning, but in this case no one is concerned with the question of what will happen to the article after 10, 20 and more years. That is why at the All-Union Institute of Restoration Research investigations were carried out to determine the influence exerted by the dry method of cleaning on museum textiles.

Tetrachloroethylene ( $\text{CCl}_2=\text{CCl}_2$ ) has a number of advantages over other solvents: it does not wash the dye off the textile, it is explosion-proof, incombustible and rather widely used in restoration practice.

One of the main criteria, determining the possibility of using tetrachloroethylene to clean museum textiles, is the ascertained residual quantity of the solvent on the textile after the cleaning. We used the mass-spectrometric method for this purpose. XVIII-XIX cc. museum textiles of vegetable and animal origin were chosen for the investigation.

The samples of fabrics were treated under the same conditions with tetrachloroethylene during 20 min, dilution ratio 1:20, temperature 20°C. The samples were then dried in air for 1 h and introduced into the mass spectrometer. The "Varian MAT-44" (USA) mass spectrometer was used, with a system of direct sample insertion into the ion source in the 20-200°C temperature range and a constant temperature gradient for all the samples (2°/min). The energy of ionizing electrons was 70 eV.

The presence of tetrachloroethylene and of the possible products resulting from its interaction with the textile fibres was determined by the intensity of  $[\text{Cl}]^+$  m/z 36 ions relative to the intensity of  $[\text{Cl}]^+$  m/z 34 ion.

In all cases, within the whole studied temperature range, the relative intensity of ions in the samples treated with tetrachloroethylene practically did not differ from the intensity of the same ions in untreated samples.

The only exception was one sample of untreated museum cotton cloth where a sharp increase in  $[\text{Cl}]^+$  ion intensity was observed at a temperature of 110-150°C. This was evidently caused by the initial sample having been contaminated with chlorine-containing compounds of unidentified nature.

At the second stage of our investigations, samples of museum and similar modern fabrics, untreated and treated under the same conditions, were subjected to ageing by insolation. Insofar as the fabrics kept at museums are mainly affected by light when being displayed at a constant relative humidity and temperature, the device chosen to study the photostability of textile materials provided for controlled gas-moisture-temperature conditions. The sun imitator consisted of two xenon lamps (DKST-5000) and two quartz mercury lamps (PRK-2) placed in the body of the unit having an aluminium reflecting mirror.

Direct control of the destruction of the polymeric matter composing the textile fibres was achieved with the help of IR - MATR (multiple attenuated total reflection) spectroscopy. The

method makes it possible to analyze sufficiently massive samples of textile materials, with the natural state of the sample remaining intact.

The spectra were recorded on a UR-20 spectrophotometer (K. Zeiss, GDR) with a MATR attachment, on a KRS-5 crystal. The IR spectra of museum and modern fabrics, untreated and treated with tetrachloroethylene, were studied after 12, 24, 36, 48 hours of insolation in the 800-4000  $\text{cm}^{-1}$  range and a change in their strength.

Destruction of all the studied kinds of fabrics after insolation is clearly reflected in an increase in the intensity of the absorption bands: for the fabrics composed of fibres of animal origin - wool and silk - in the 1650 and 1560  $\text{cm}^{-1}$  bands, answering to amide bonds in the primary and the secondary position /1/; for the fabrics composed of fibres of vegetable origin - for C=O bonds in the 1725  $\text{cm}^{-1}$  band, corresponding to the bonds between pyranoid rings, and C=C bonds in the 1660  $\text{cm}^{-1}$  band, characteristic of the bonds of pyranoid rings with their side groups /2/.

The changes in band intensity, depending on the molecular masses of the compounds composing different fibres, are associated in a different way with the changes in their strength. For keratin and fibroin, whose molecular mass does not exceed  $10^5$  g and decreases under the action of the solvent, large decreases in strength are observed. For cotton cellulose, with molecular mass greater than  $1.5 \times 10^6$  g, this decrease is smaller. In some cotton fabric samples the strength is noted to increase after insolation, as the molecular beams in this case, changing their orientation, decrease the angle of inclination to the fibre axis. However, any decrease in the molecular mass after new insolations affects the textile longevity.

The investigations performed lead to the conclusion that tetrachloroethylene exerts an unfavourable effect on all the kinds of textiles in question. In the museum textile samples treated with tetrachloroethylene the destruction process goes faster than in the untreated ones, and the treatment of modern textiles models the destruction process. Therefore, the final decision on the choice of the method of cleaning museum textile materials and on the expediency of using tetrachloroethylene must be made after estimating and taking into account the state of the exhibit preservation.

#### References

1. R. Meredith, J. Hurl. The Physical Methods of Studying Textile Materials. (Transl. from Eng.). Gizlegprom, 1963.
2. R. L. Feller, S. B. Lee and J. Bogaard. The kinetics of cellulose deterioration. In: Historical Textile and Paper Materials. Conservation and Characterization. American Chemical Society, Washington D.C., 1986, p. 329-347.



## RESUME

L'article concerne le problème de renforcement des tissus en question en drap, de velour, de drap et de feutre. On offre une nouvelle technique de renforcement des tissus en question utilisant des matériaux non-tissés thermocollables du type de "toile d'araignée" et fait l'analyse des inconvénients et des avantages des méthodes de renforcement des tissus telles que le masticage, la méthode traditionnelle - à l'aide du fil et de l'aiguille - et le doublement sur des matériaux thermocollables. On envisage aussi le problème concernant la résistance des fibres de soie et de laine en fonction des variations de température. L'article donne aussi quelques exemples de restauration pratique.

## LA RESTAURATION DES TISSUS AVEC L'UTILISATION DU MATÉRIAU NON-TISSÉ THERMOCOLLABLE DANS LES MUSÉES DU KREMLIN DE MOSCOU

I.M.Katchanova  
Musée d'Etat du Kremlin de Moscou

Les musées d'Etat du Kremlin de Moscou possèdent une grande collection de vêtements faits en drap et en feutre. Une partie de vêtements en question est exposée au Palais des armures, mais le gros de la collection se trouve dans les fonds du musée. Malheureusement, nombre de ces vêtements sont en mauvais état de conservation, ce qui avait été signalé encore à la fin du XVIII siècle dans les anciens registres du Palais des armures. Dans ces documents, après la description de tel ou tel objet de vêtement d'apparat de tsar ou de courtisan (ceci concerne surtout les vêtements en drap ou en feutre) suit la mention "attaqué par les mites" ou "attaqué par les mites, absolument vétuste, en morceaux".

Jusqu'à présent, il était extrêmement rare que de tels vêtements soient donnés en restauration, ce qui était, en règle générale, conditionné par l'absence des méthodes appropriées qui auraient permis de les restaurer rapidement et avec une bonne qualité ou de les conserver.

Le renforcement des tissus présentant de nombreuses pertes de grandes ou petites dimensions par la méthode traditionnelle - à l'aide du fil et de l'aiguille - demande beaucoup de travail. Vu un très grand nombre de vêtements nécessitant les soins de conservation et un nombre très restreint de restaurateurs qualifiés, il n'est pas acceptable de dépenser beaucoup de temps pour ce travail de conservation.

Les musées de l'Union Soviétique possèdent également une certaine expérience en matière de restauration des objets en drap et en feutre par le procédé de masticage. En recourant à cette méthode on procède de façon suivante: les petits morceaux du tissu de laine, teints de la même couleur que l'objet à restaurer, sont réduits en duvet et mélangés avec de la colle de farine, lequel mélange est ensuite appliqué dans les endroits abîmés /1/. Cependant, le temps a mis en évidence toute l'imperfection de cette méthode: après un certain temps la colle se dessèche, les fibres de laine partent et les trous deviennent à nouveau visibles. D'ailleurs, cette méthode présente également un défaut purement esthétique, puisqu'on perd ainsi l'intégrité de la perception visuelle du monument. L'objet exposé se parcelle: en premier lieu on voit un grand nombre de pertes de grandes et petites dimensions camouflées avec une grande maestria. A cet effet, il faut rappeler que l'objectif final de la restauration ou de la conservation consiste à conserver et à révéler le tissu d'origine et, en même temps, à rendre à l'objet sa forme initiale et l'intégrité de la perception. Cet objectif peut être acquis grâce à une opération très délicate de refixage du vieux tissu sur un nouveau support doublé.

Il est nécessaire de mettre au point des méthodes qui assureraient une haute qualité du travail de restauration ou de conservation et des dépenses minimales du temps. Les méthodes en question doivent être technologiques, convertibles, non-nocives pour la santé du restaurateur.

La section de restauration et conservation scientifiques des musées d'Etat du Kremlin de Moscou même le travail de recherche de telles méthodes. Notamment, pour doubler les vêtements en tissu de laine, en velour et en feutre il est proposé d'utiliser en qualité de matière collante les matériaux non-tissés thermocollables du type de "toile d'araignée" /2/.

Avant de proposer cette méthode pour l'utilisation pratique, on a procédé à des essais de laboratoire complexes, qui comprenaient l'étude des modifications des propriétés physiques et mécaniques des tissus (rigidité, solidité du collage, couleur, brillant, etc.), ainsi que des modifications de la structure chimique des fibres naturelles de laine et de soie. Les essais étaient faits sur des échantillons de vieux tissus pris aux fonds auxiliaires du musée. Toutes les modifications étaient étudiées dans les conditions du vieillissement artificiel par la lumière et par la chaleur /3/.

Les essais ont permis de constater que l'utilisation, en qualité de la couche collante, de la toile d'araignée de différentes



densités linéaires permet:

a) d'exclure la formation d'une pellicule continue du polymère entre les tissus doublés, de régler leur propriétés mécaniques (solidité du collage, rigidité, drapé) en fonction du type de tissu et du type d'objet à restaurer;

b) d'exclure la pénétration de la colle dans la structure du tissu à restaurer et, grâce à cela, d'exclure l'effet de sa pénétration indésirable sur le côté face de l'objet exposé.

Afin de définir les domaines d'application du procédé de doublage de tissus anciens à l'aide de matériaux synthétiques thermocollables, on a procédé à l'étude de l'influence de la température sur la modification de la structure chimique des fibres naturelles de laine et de soie (à noter qu'à cette étape l'influence de la colle n'était pas prise en considération). Les modifications structurales étaient évaluées d'après la variation de la vitesse de la dissolution des fibres en fonction de l'action de la température. Les essais étaient effectués conformément aux méthodes utilisées pour l'étude microchimique des fibres textiles /4/.

Les essais concernaient les échantillons suivants de fibres de tissus:

- I - tissu de soie vétuste (XVII siècle),
- II - draps de XVIII siècle,
- O<sub>s</sub> - fibres de soie n'ayant pas subi d'action de la température,
- O<sub>1</sub> - fibres de laine n'ayant pas subi d'action de la température,
- I<sub>1</sub> - fibres de soie après la température t = 60°C,
- II<sub>1</sub> - fibres de laine après la température t = 60°C,
- I<sub>2</sub> - fibres de soie après la température t = 70°C,
- II<sub>2</sub> - fibres de laine après la température t = 70°C,
- I<sub>3</sub> - fibres de soie après la température t = 80°C,
- II<sub>3</sub> - fibres de laine après la température t = 80°C,
- I<sub>4</sub> - fibres de soie après la température t = 100°C,
- II<sub>4</sub> - fibres de laine après la température t = 100°C.

Le degré de destruction des fibres était déterminé d'après la variation relative de la vitesse de la dissolution  $E = \frac{t_i - t_0}{t_0} \cdot 100\%$  où t<sub>i</sub> - temps de la dissolution de l'échantillon considéré, t<sub>0</sub> - temps de la dissolution de l'échantillon initial.

Les résultats des essais figurent dans le tableau ci-dessous. Le temps moyen était défini sur la base de l'étude de 10 échantillons.

Echan- tillon	Tempéra- ture du traite- ment, °C	Temps moyen de dissolu- tion, min	E (%)	Echan- tillon	Tempéra- ture du traite- ment, °C	Temps moyen de dissolu- tion, min	E (%)
O <sub>s</sub>	0	3,06	-	O <sub>1</sub>	0	5,34	-
I <sub>1</sub>	60	2,30	19,0	II <sub>1</sub>	60	5,32	0,59
I <sub>2</sub>	70	2,26	21,5	II <sub>2</sub>	70	5,28	1,79
I <sub>3</sub>	80	1,46	43,0	II <sub>3</sub>	80	5,25	2,69
I <sub>4</sub>	100	1,43	44,6	II <sub>4</sub>	100	5,19	4,49

Les essais ont permis de constater que l'action de la température provoque une baisse sensible de la résistance mécanique des fibres constituant le tissu de soie vétuste: plus élevée est la température du traitement thermique, plus importante est la baisse de la résistance des fibres. La modification de la résistance des fibres de laine sous l'action de la température est négligeable.

Ainsi, le procédé de doublage par thermocollage ne peut pas être appliqué à tous les tissus sans distinction. Le procédé en question n'est pas applicable, si l'action de la température provoque une baisse importante de la résistance mécanique des fibres constituant le tissu, comme ceci a lieu dans l'exemple ci-dessus. Il paraît que dans chaque cas concret il faudrait procéder à une analyse microchimique préalable et, d'après le degré de la baisse de la résistance mécanique des fibres, faire la conclusion sur la possibilité de l'utilisation du procédé de doublage par thermocollage du tissu considéré.



Les essais ultérieurs étaient orientés sur l'étude des changements structuraux des fibres constituant le tissu pendant le processus du vieillissement artificiel par la lumière et par la chaleur. A cet effet on a recouru aux méthodes de la spectroscopie à infra-rouges, de la radiographie aux rayons X, de l'analyse microchimique.

On a procédé à une analyse comparative des fibres du tissu doublé par la toile d'araignée thermocollable, vieilli et, par la suite, à nouveau séparé de la toile d'araignée thermocollable avec les fibres de ce même tissu, mais qui n'a pas été soumis à l'opération de doublage. Les résultats ont démontré que les changements qui se produisent pendant le processus du vieillissement dans la structure du tissu non-doublé sont identiques aux changements qui se produisent dans les fibres du tissu doublé, vieilli et, par la suite, séparé de la toile d'araignée thermocollable. Dans d'autres termes, le matériau polymère collable, utilisé pour le doublage, n'exerce aucune influence négative sur les processus du vieillissement naturel des tissus. Tant qu'on n'aura pas mis au point des impregnants de conservation spéciaux pour ralentir le processus du vieillissement naturel des tissus qui ne provoqueraient pas de changement de l'aspect extérieur des tissus, l'introduction des substances étrangères dans la structure des tissus encore suffisamment résistants et vivants est indésirable.

Ainsi, l'aspect théorique de la possibilité d'utiliser la toile d'araignée thermocollable pour le doublage des tissus, notamment ceux de laine, a été confirmé par voie expérimentale.

Le procédé de doublage proposé présente un certain nombre d'avantages en comparaison avec les procédés connus.

1. En fonction de l'épaisseur et de la densité linéaire du matériau non-tissé thermocollable, il est possible de faire varier la rigidité du tissu à restaurer. Ainsi, par exemple, à la restauration des couvre-chefs, lorsqu'il faut rétablir la forme perdue et la rigidité dans les endroits abîmés, il est possible d'utiliser le matériau collable constitué par les fibres thermocollables de grand diamètre et de densité linéaire plus élevée (on peut également utiliser plusieurs couches de toile d'araignée thermocollable mince).

En cas de tissus de laine minces, notamment de vêtements, où il faut éviter une rigidité trop grande, il est possible d'utiliser la toile d'araignée thermocollable mince. Dans ce cas, après le doublage, entre les tissus ne se forme pas une pellicule continue de polymère, qui accroît la rigidité. La fixation est régulière et suffisamment solide.

2. La méthode en question est technologique, autrement dit, elle permet de réaliser un doublage de qualité et d'exiger pas d'opérations auxiliaires supplémentaires qui consistent à fabriquer le châssis, à tendre le tissu à doubler sur le châssis, à enlever le tissu du châssis après l'application de la colle, etc. La méthode ne présente aucun danger pour la santé du restaurateur. L'application par pulvérisation de la colle dans les endroits où la rigidité a diminué présente le danger de la pénétration des particules du polymère dans les voies respiratoires du restaurateur.

La qualité du doublage s'accroît, grâce au fait qu'il est possible d'éliminer la colle dans les endroits à restaurer avant de procéder au fixage du tissu de l'objet à restaurer sur le support de doublage. Dans ce cas, la solidité du collage aux limites des endroits à restaurer reste bonne et la colle ne pénètre pas sur la surface du tissu à restaurer (à la différence des procédés connus dans lesquels la colle doit être enlevée des endroits à restaurer à l'aide du solvant, mais ceci après le doublage des tissus) /5/.

En outre, dans le procédé proposé l'action thermique s'applique du côté du support de doublage, ce qui assure une répartition plus régulière de la température et de la pression sur la surface du matériau collable, puisque ce dernier se trouve plus près de la surface chauffante. En vue de doubler les objets exposés, on choisit, en règle générale, un support de doublage présentant une facture plus raréfiée et plus mince.

Un autre avantage du procédé de doublage de l'envers consiste à ce que le côté face de l'objet à restaurer n'est pas exposé à l'action directe de la surface chauffante, laquelle action étant susceptible de provoquer l'écrasement et la destruction des fib-



res, le pliage des poils sur le tissu de l'objet. D'ailleurs, les couches du tissu de doublage, du matériau collant et l'épaisseur du tissu de l'objet à restaurer lui-même contribuent à la baisse de la température à l'approche du côté face de l'objet à restaurer, ce qui est préférable pour la conservation de l'aspect extérieur et de la résistance du tissu à restaurer.

A l'application de la méthode proposée et à condition de bien choisir le tissu formant le support de doublage, il est possible de procéder à la conservation ou à la restauration rapides et de bonne qualité de l'objet exposé, ou de rétablir, si nécessaire, sa forme initiale.

3. La méthode proposée est convertible, puisqu'il est possible d'enlever le support de doublage ensemble avec la colle, ce qui permet d'exclure une dissolution totale du polymère et sa pénétration dans la structure du tissu.

Pour la première fois, la nouvelle méthode a été utilisée à la restauration de la reliure en velours de l'Evangile faisant partie de la collection du Palais des armures.

Lorsqu'on a reçu l'Evangile pour la restauration, le problème s'est posé de remplacer le velours vétuste de la reliure qui a totalement perdu son aspect initial par un velours nouveau. De ce fait, il a été décidé d'essayer la nouvelle méthode de doublage. Après avoir éliminé les tâches du cire et procédé à un nettoyage total du velours à l'aide de l'eau, on a collé le velours d'origine sur un support de soie fine à l'aide de la toile d'araignée thermocollable. L'utilisation de la méthode a donné de bons résultats, ce qui a permis de la recommander pour la restauration de l'un des chapeaux en feutre.

Pour rendre leur aspect initial aux objets relativement petits (par exemple aux chapeaux), mais présentant de grands trous et, de ce fait, ayant perdu leur aspect et forme initiaux, il est possible de les restaurer, ce qui signifie dans ce cas de combler les trous avec un tissu présentant une facture et une couleur proches de celles du tissu d'origine. Comme exemple, on peut citer les travaux de restauration du chapeau qui avait appartenu à Pierre II (XVIII siècle). Le chapeau en question était dans un très mauvais état: totalement déformé, taché de la colle ancienne et présentant des trous assez grands.

Après avoir démonté la doublure, enlevé les couches anciennes de la colle et procédé à un nettoyage général à l'eau, on a comblé les trous de deux côtés avec le tissu de facture et de couleur proches à celles du tissu d'origine. A cet effet on a utilisé du feutre de pure laine de couleur noire. Afin de rendre au chapeau sa rigidité perdue dans les endroits des trous, on a choisi en qualité du matériau collant la toile d'araignée thermocollable présentant une densité linéaire suffisamment grande.

Après que les trous soient comblés de deux côtés et la rigidité soit rétablie à l'aide du matériau collant, le chapeau a repris son aspect extérieur et sa forme d'origine.

Un autre exemple d'utilisation du procédé de doublage sur la toile d'araignée thermocollable est le travail de conservation de l'habit de chambellan du XVIII siècle, fait en drap noir. Dans son ensemble, l'habit était en état relativement bon et n'avait pas perdu sa forme initiale. Cependant, une multitude de petits trous nuisaient considérablement à son apparence d'exposition. La fixation des endroits abîmés a été effectuée sur un support mince en tissu de laine de couleur noire. Le doublage à l'aide de la toile d'araignée était effectué par fragments, dans les zones de concentration des trous. L'habit a repris son apparence d'exposition. Les travaux de conservation ont été effectués dans un temps très bref.

#### Bibliographie

1. Solovieva I.I. Le masticage des tissus attaqués par les mites. Informations du VTzNILKR, 1967, vol. 19, p. 55-61.
2. Katchanova I.M. La possibilité d'utiliser les nouveaux matériaux et méthodes de doublage pour la restauration des tissus de musée. Restauration et conservation des valeurs culturelles. Recueil d'exposés scientifiques, Informkouloura, 1981, vol. 6.
3. Makarova T.A., Litovtchenko S.F., Katchanova I.M. L'influence des procédés de doublage des tissus sur leurs caractéristi-



ques physiques et mécaniques, Nouvelles des Ecoles Supérieures, Tekhnologuia tekstilnoj promychlennosti, 1984, n° 1, p. 16-19.

4. Bobet V. L'utilisation pratique des méthodes de microgonflement et de dissolution aux essais des matériaux textiles. Nouvelles des Ecoles Supérieures. Tekhnologuia tekstilnoj promychlennosti, 1960, n° 4, p. 13-28.

5. Leene S. Textile conservation. London, 1972.





## SUMMARY

The conservation of the base fabric of a Caucasian shadda flatwoven carpet provided an excellent opportunity to study the weaving technique of this group of carpets. The rather worn and broken parts of the original textile were conserved, and the missing segments of the edge were completed using the unusual method of drawing the warps - in lengths of approximately 4 cm - into the reverse side only under every second weft. In addition, the warps were left floating openly on the back side of the carpet instead of weaving them back into the textile. These methods had two advantages; 1./ the textile was not substantially thicker than the original upon completion, and 2./ the alterations made on the carpet were reversible.

# CONSERVATION AND COMPLETION OF AN EARLY 19TH-CENTURY CAUCASIAN SHADDA FLATWOVEN CARPET

Györk Mátéfy

National Centre of Museums

Budapest 100, P.O.B. 54. 1476 Hungary

## Description of the carpet

The early 19th-century Caucasian shadda flatwoven carpet /185 x 190 cm/ belongs to the collection of the Museum of Applied Arts of Budapest, Hungary. A chainpatterned ornamentation borders the carpet; rows of camels with small animal, plant, and human figures comprise the decoration. The dyes used in the carpet are blue and red; the patterns are woven with blue, red, yellow, brown, and natural coloured wool yarns. The weaving technique is the so-called shadda which is explained in various ways in the literature /1, 3, 4, 5, 6, 7/. In this case the weaving technique is palas, and the patterns are woven with soumak and jijim techniques /see Figs. 5 and 6/.

## Description of condition before conservation

The warps and wefts were well worn on the right side of the carpet. There was a large hole on the left side, and the left edge was incomplete /Fig. 1/. Many warps and wefts were broken, giving the appearance, at first glance, of faulty weaving. When the textile was moved, the broken thread ends slipped into the unbroken base fabric, thus exacerbating the difficulty of the challenge. To minimize this additional damage, it was necessary to secure these



Fig. 2: Secondarily knotting of warps

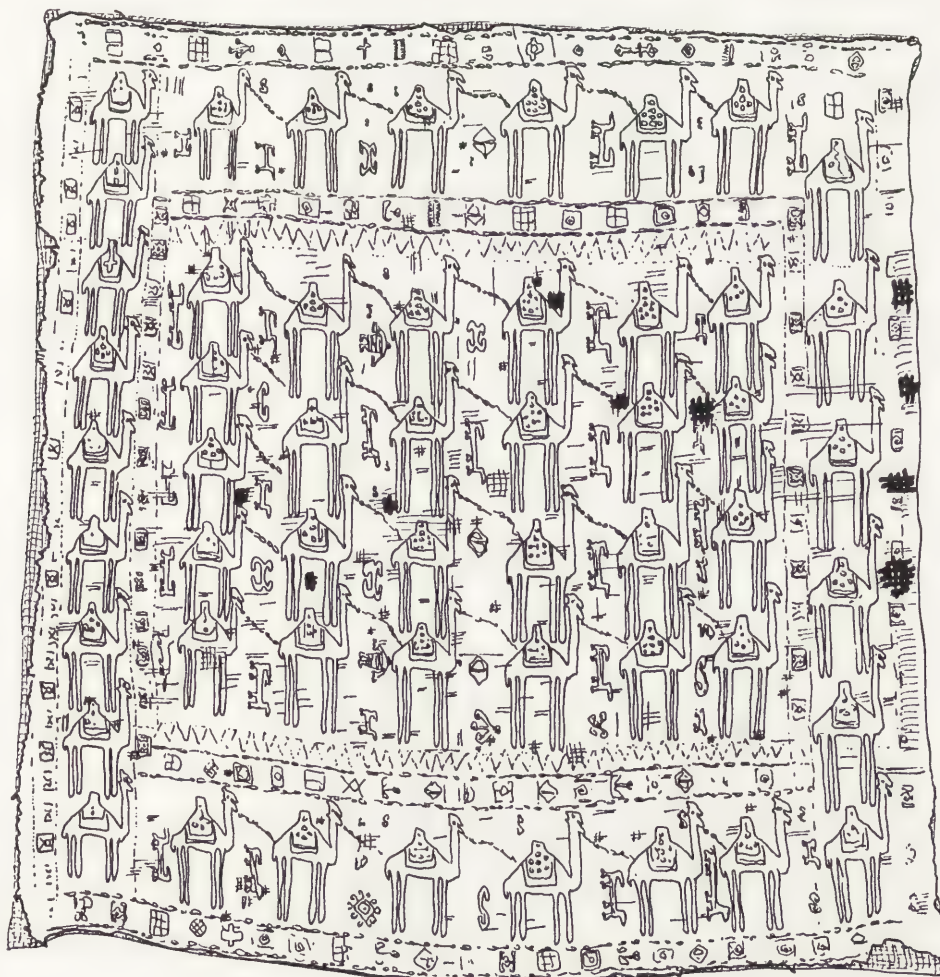


Fig. 1: Design of the carpet:

- 1 ≡ worn-out or broken warp or weft;
- 2 # hole, broken or incomplection;
- 3 \* untying, discoloured older completion



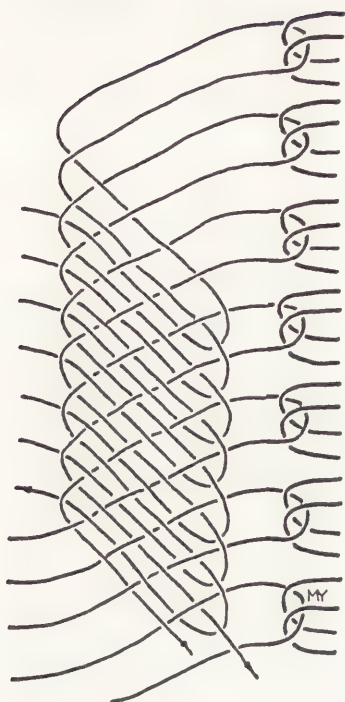


Fig.3: Interweaving of warps

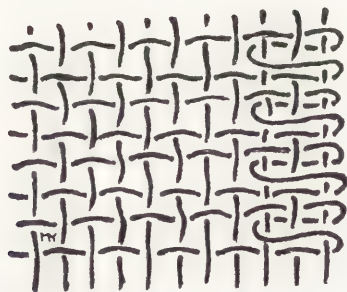


Fig.4: The original woven-edge



Fig.5: Weaving in soumak-technique

broken thread ends. The base fabric of the carpet was abraded and incomplete in places; the frayed edges were stitched together with black thread. Previous repairs made on the red coloured ground had turned yellow in color in eleven places.

On the left edge, a 5-8 cm strip was frayed for almost the entire length. Loose warp ends were turned back and secured to the original weave /see Fig. 2/.

The right edge of the carpet was basically intact except for minor areas which required some repair /see Fig. 3/.

The woven edges /Fig. 4/ were also incomplete. After removing some of the previous repairs, it was obvious that these areas required additional conservation.

The motifs of the carpet were woven using soumak /Fig. 5/ and jijim techniques /Fig. 6/ into the palaswoven base fabric. As a result of these weaving techniques, the surfaces of the relief motifs were abraded and revealed losses. Restoration of the motifs was aided by the fact that their contours were clearly identifiable. On those parts of the carpet damaged to the extent that the base fabric required reweaving, a decision was made on the advice of curators, not to attempt completing the motifs.

#### Investigation of materials

The fibres of the textile were examined under the microscope and using burning, and dissolving tests /8/. The warps, and wefts, as well as the blue, red, yellow, and brown dyed yarns were wool, whereas the natural coloured yarns were cotton.

Dyes were identified using thin-layer chromatography /9, 10/ and indigo tests /11/. The results indicated that the red yarn was dyed with madder /*Rubia tinctorum*/. The yellow threads were dyed with weld /*Reseda luteola*/, and the blue with indigo /sometimes on natural brown wool/. The brown dyes contained tannic acid. The cotton yarns were not dyed.

The base fabric in which the warps and wefts were interlaced equally was woven with 2-ply, S-twisted wool threads of equivalent thickness. The threads comprising the pattern were likewise made of 2-ply, S-twisted wool and cotton threads.

#### Conservation

The carpet, frequently on display, had been cleaned in the workshop of the Museum of Applied Arts. The eleven faded patches - originally red in color - were removed and newly restored. The three different wool threads used for completing the carpet were 30/3, 12/3, and 3/2, S-twisted threads. Acid dyes were used to obtain the appropriate colours. The several broken segments were stitched with very fine wool thread using conservation stitches.

Completing the missing left edge presented the greatest problems because the usual method for weaving the warp into the loose base fabric would have made that area considerably thicker, even causing the fabric to lose its original drape.

I decided, therefore, to let the warp ends float freely on the reverse and not to weave them into the textile under every weft. Curators questioned but ultimately accepted this unusual conservation method. In my opinion, this method has two advantages: the completed portion is not substantially thicker than the original, and the method of treatment is reversible.

Repairing the warp thread damage on the left edge proceeded as follows:

- 1./ The broken edge was reinforced with conservation stitches;
- 2./ The warps were finished by:
  - a./ After 3-4 weft-lines, the warp threads were drawn into the reverse-side under every second weft - in lengths of approximately 4 cm - /Fig. 7/, in such a way that warp threads moved away a weft-line each. This method avoided undesirable thickening of the textile along this edge;
  - b./ As the next step, the warp threads were turned back at the edge to form a U-shape, similar to the original segment, leaving the ends of the warp threads floating inwards on the reverse-side of the carpet;
- 3./ The new warp threads were used to weave the missing segments;
- 4./ Finally, a thicker wool thread was passed through the 2-2 loops into the new warp thread loops according to the original method of manufacture /Fig. 6/. This specific method imitated the original technique.





Fig.6: Weaving in jijim-  
technique



Fig.7:  
1 The base fabric  
2 The conserving stitches  
3 Completion of warps

For exhibition purposes, a strip of Velcro was stitched onto the back upper edge of the carpet.

#### References

1. F. Batári, "Keleti szőnyegek. - Szövött szőnyegek", in Régiségek könyve, ed. P. Voit /Budapest: Gondolat, 1983/ pp. 444-445.
2. T. Efendiyev, "Techniques and Methods of Carpet Restoration at the Azerbaijan Centre for Scientific Restoration of Museum Exhibits", Hali 6, no. 3 /1984/ pp. 272-275.
3. V. Enderlein, Orientalische Kelims. - Flachgewebe aus Anatolien, dem Iran und dem Kaukasus /Berlin: Kunst u. Ges., 1986/ pp. 99, 157-158.
4. K. Gombos, "Kaukázusi népek szövött szőnyegek a budapesti Iparművészeti Muzeumban", Művészet, no. 1 /1978/: pp. 22-25.
5. K. Gombos, "Régi szövött keleti szőnyegek és himzések", Vas megyei muzeumok katalógusai, no. 66.
6. L. Kerimov et al., Rugs and Carpets from the Caucasus. - The Russian Collections /Middlesex: Penguin, Leningrad: Aurora, 1984/ pp. 28-29.
7. A.N. Landreau, W.R. Pickering, From the Bosphorus to Samarkand /Washington: The Textile Museum, 1969/ p. 97.
8. T. Szentpály, R. Szentpálné Leitner, Textiliák kémiai vizsgálata /Budapest: Műszaki K. / p. 278.
9. J.H. Hofenk de Graaff, "On the Occurrence of Red Dyestuff in Textile Materials from the Period 1450-1600" /Paper delivered at the Plenary Meeting of the International Council of Museums Committee for Conservation, Madrid, October 2-5, 1972/, p. 35.
10. J.H. Hofenk de Graaff, W. Roelofs, "The Analysis of Flavonoids in Natural Yellow Dyestuffs Occurring in Ancient Textiles" /Paper delivered at the Fifth Triennial Meeting of the International Council of Museums Committee for Conservation, Zagreb, September 4, 1978/, p.15.
11. J.H. Hofenk de Graaff, "A Simple Method for the Identification of Indigo", Studies in Conservation 19, 1974: pp. 54-55.





## SUMMARY

This project was set up to deal with about 2,000 medieval textile fragments, which had received conservation treatment 10-15 years ago and required re-assessment and mounting to minimize handling.

Conservation treatment was limited to removing previous lubricants, which were not preventing wool particles from being shed, some wet-cleaning, and humidification to flatten the fragments.

The mounting of the textiles is described step by step, including adaptations for thicker fragments, fragile items, and window mounts. Acid-free boards with a cut-out containing each fragment were placed in a Melinex sleeve, and then stored in boxes. This method enables the textiles to be safely housed, to be visible without being disturbed, and accessible for study.

# THE TREATMENT, MOUNTING AND STORAGE OF A LARGE GROUP OF ARCHAEOLOGICAL TEXTILE FRAGMENTS

Lynn Morrison  
Conservation Officer  
Museum of London  
London Wall  
London EC2Y 5HN  
England

## Introduction

During excavations on the Baynards Castle site in the City of London during 1972, a large quantity of medieval textile fragments were found in three waterlogged dumps dating from the mid-14th to the 16th century (1). The anaerobic burial conditions of the river-front had resulted in excellent preservation of a range of organic materials which included leather, hair, vegetable fibres, and the wool and silk textiles. Post-excavation treatment of the textiles consisted of initial cleaning in water to remove mud and debris, then later more specialised treatment in laboratories from 1972 to 1975 (2).

The importance of a unique collection of some two thousand textile fragments from a well-dated context was recognized, and cataloguing, technical examination and scientific analysis began (3). Additional research work was hampered by the condition of the textiles, which had not been mounted but were crumpled and folded in small polythene bags (fig. 1). Increasing interest and handling were leading to deterioration of the fragments, some of which were very fragile; it was clearly necessary to mount the textiles as well as study them. Accordingly, funds were raised for a one-year project which commenced in 1986. Its aims were to arrest damage to the textiles by suitable mounting, to make them flat and clearly visible for study yet ensure that they could be viewed with a minimum of handling, and to store them in a standardized system of containers so that they were accessible but did not take up a great deal of space. During this process, the condition of the textiles themselves could be re-assessed and further conservation treatment carried out as required.

## Conservation of excavated textiles

A brief description of the textiles indicates their range and inherent interest. They were primarily wool, with some silks and mixed fibre fabrics, and included numerous examples of different weaving techniques and pattern and colour effects. Construction was evident in surviving seams, stitches, darts and buttonholes. As well as pieces of clothing, there were also miscellaneous items such as braids, cords, garters, small bags and part of a hat.

The condition of the wool textiles was creased and crumpled, which made examination difficult. Some of the pieces still had soil adhering to them, and a few were disfigured by concretions. They had retained reasonable flexibility but the fibres were

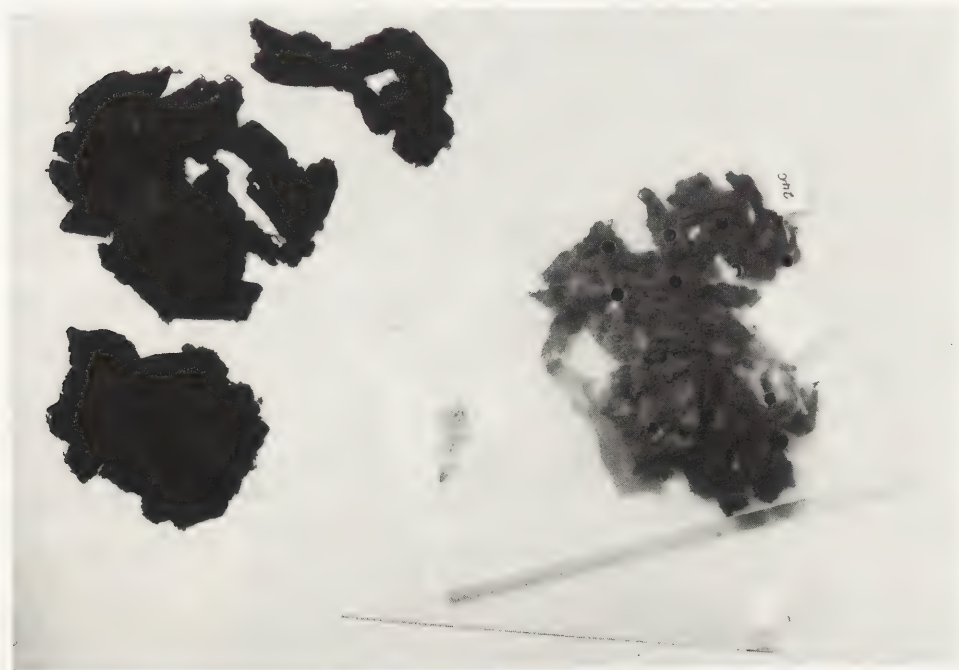


Figure 1 - the textiles as received

degraded and brittle causing particles to be shed. Under the microscope at a magnification of x 100 the cuticular scales could be seen to be severely eroded. On ageing wool protein loses some of its sulphide linkages and therefore a percentage of its mechanical strength (4), and it would seem that this embrittlement and shedding of fibres is irreversible, particularly in the case of excavated textiles. Earlier conservation had sought to avoid embrittlement by the use of lubricants (2), but fragments in this collection were brittle when examined ten to fifteen years later. In addition, they were dark with surface detail somewhat obscured there was a definite odour and stickiness, and it is possible that the dressings could attract dust and micro-organisms.

The proposed treatment was therefore to first consider the possibility of using a lubricant in order to increase flexibility or a consolidant to minimize further fibre loss, while assessing the effect of previous dressings on the rate of shedding; to remove soil and concretions if necessary; and finally to flatten and remove creases prior to the final objective of mounting the textiles.

The literature on lubricants revealed there is some confusion between the use of consolidants to increase tensile strength and lubricants to ensure flexibility. The aim in this case was to prevent further loss of fibres and whilst it would be desirable to find a lubricant that imparts both flexibility and strength, it would appear that this remains an ideal rather than a practicable proposition at present.

Products that have been used as lubricants include fabric conditioners (quaternary ammonium compounds which are a form of cationic softener), oils such as lanolin (a naturally-occurring wool fat), glycerol, polyethylene glycol, Bavon, as well as recipes consisting of mixtures of oils, waxes and humectants in solvents. Lubricants investigated by Delacorte *et al* were found to impart flexibility and sometimes tensile strength, especially glycerol. "However after three weeks of accelerated ageing the beneficial effects of all of the lubricants essentially disappeared", it was stated, and after the evaporation or oxidation of lubricants, the textile may be left weaker than if it had never been treated (5). It appears therefore that experimental work so far does not provide clear cut evidence as to the benefits of using lubricant treatments.

In the long term, the effects of chemical residues in fibres is not known, and therefore the decision was taken to dissolve and remove the old dressings using two baths of Genklene (1,1,1-trichloroethane) of between one and five minutes each. Following the principle of minimum intervention, it was felt that there was no advantage in re-wetting the textiles and adding further lubricants, but that it was preferable to design a supportive mounting system that minimized handling and consequent shedding of particles.

The next step in the conservation treatment was to wet-clean those pieces that still had soil adhering, as dirt can be acidic and abrade fibres causing damage. These were washed gently in deionized water and about 0.2% Synperonic N (a non-ionic detergent using almost no mechanical action. If the fragments were particularly fragile they were sewn between net for support. All were rinsed and allowed to air dry. Washing was found to improve lustre and flexibility of the fibres, but had no effect on the concretions adhering to the textile. It was not possible to remove these using a scalpel under the microscope as this cut through the attached fibres, and dissolving concretions with drops of dilute acid similarly destroys fibres, so no attempt was made to carry out these operations.

Before mounting, all wool textiles were humidified overnight by being laid out under slight pressure on cloths sprayed with deionized water. This ensured that the fibres were relaxed and the fragments could be unrolled, the creases removed, and they were flat enough for mounting. Silks could be wetted on glass and after the fibres were aligned and the fragments were straightened, they could be left to air dry.

#### Some factors to be considered in mounting and storage

If textile fragments are essentially two-dimensional, it is necessary that they are mounted flat and fully extended, unless they are so large that they must be stored rolled up. They should be accessible yet protected from light, fluctuations in relative humidity, dust, pollution and insect pests. Another requirement is that the items are physically supported against movement yet are



easily visible so that they do not have to be handled or physically disturbed to be seen.

The number of textiles, funds and time available will largely dictate a methodology. Other factors to be borne in mind include cost and availability of mounting materials, ease of making mounts and storage containers, hazardous methods or materials employed, and whether the textiles will be displayed or stored, and if the latter, how much space is available. Once a mounting and storage system has been decided on, it is helpful to order all the materials and containers of a standardized size, and multiples of this, for efficiency in carrying out the process and ease of storage.

There are many methods for mounting small textiles in a frame or onto fabric, hardboard, perspex or acid-free board (6). Without going into detail, it can be seen that some of these methods are theoretically sound but in practice they are often enormously time-consuming. Their very ingenuity makes them too complicated to carry out on a large scale. Some mounts do not employ readily available, inexpensive or chemically inert materials with long-term stability. A method which meets the above requirements was developed based on acid-free card which holds the textile in a polyester sleeve, stacked flat in boxes, and this is described below. Crucial to the method devised was the use of a suitable adhesive that would avoid build-up of harmful vapours in the microclimate created by the packaging of the textiles, and a limited number of adhesives were investigated. Other criteria applied included flexibility sufficient to allow the mounts to flex, good ageing properties, and whether the adhesive was solvent-based or not. A solvent-based adhesive was considered more suitable than a water-based emulsion, such as the polyvinyl acetates, as this would not wet the card and cause it to become cockled or stained.

Some tests were carried out in the laboratory on Klucel G (7), a hydroxypropyl cellulose ether manufactured by Hercules, which has the advantage of being soluble in both water and alcohol. Klucel G was found to have excellent long-term ageing properties, remaining flexible and unyellowed for a comparatively long time in accelerated ageing tests under ultraviolet light and in the oven (8). It was found to be reversible, and it was not susceptible to attack by micro-organisms even in very high relative humidity. It is already used extensively on organic materials both as a consolidant and an adhesive.

A 5% solution was made up in industrial methylated spirits in a fume extraction cupboard. The easiest method of dissolving Klucel is to pour the powder slowly into the vortex created by a flat-spin in the liquid of a beaker placed on an electric stirrer. If full dissolution does not occur immediately, the beaker should be sealed and stirred occasionally over a period of a few days. In order to give the preparation more 'tack', it was mixed with 5-10% Vinamul 3252 (9), a polyvinyl acetate chosen for its superior long-term ageing characteristics and its great flexibility which gives it considerable elastic stretch even on ageing. Further work is being carried out on this adhesive mixture and on mounts made up using it to test its qualities over time. This adhesive proved effective on all the materials used in the mounting process, and the procedure is described below.

#### Mounting and storage system for the Baynards Castle textiles

After conservation treatment, the textile fragments were laid out singly or in groups on museum board (4-ply acid-free card) which measured 261 mm by 323 mm; boards twice the size were available for the larger pieces. Their outlines were traced in pencil and museum accession numbers were written alongside in Indian ink.

The shape of the fragments was then cut out using an electric fretsaw with a fine blade (fig. 2), and any rough edges smoothed with fine sandpaper. This enables quite intricate shapes to be cut out with speed and precision, and is a useful and inexpensive piece of equipment when large quantities of mounts are to be tackled. For smaller projects, a scalpel or Stanley knife can be used to cut out the shapes. This board was then stuck down onto another board (fig. 3) using Klucel G 5% in industrial methylated spirit with 5-10 Vinamul 3252 added, and a sheet of weighted glass left overnight on each board was enough to ensure a good bond. Thus, a recessed well was provided for each fragment to lie in (fig. 4).

An option to view the whole or part of a piece from the reverse was provided in a number of cases. Window mounts were made by cutting a piece of Melinex (10) slightly larger than the fragment, and

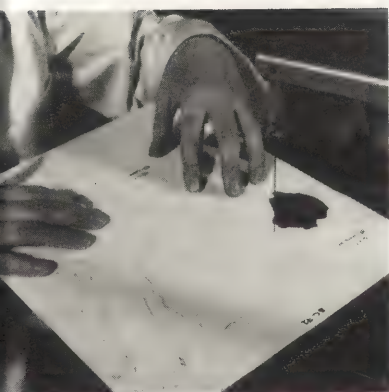


Figure 2 - cutting out shapes on a board using electric fretsaw

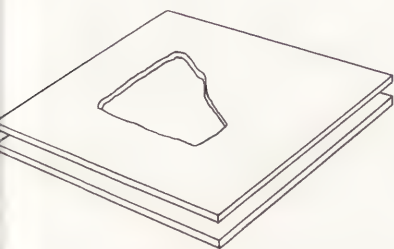


Figure 3 - board with cut-out being placed on back board

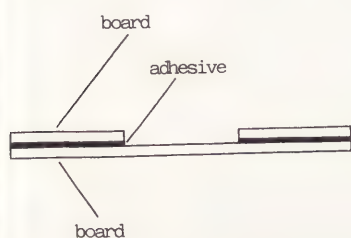


Figure 4 - cross-section of boards





Figure 5 - window mount

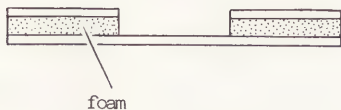


Figure 6 - cross-section of foam core board

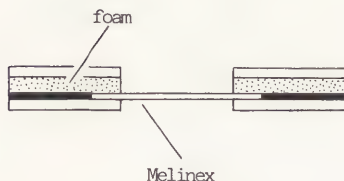


Figure 7 - cross-section of foam core board with window mount

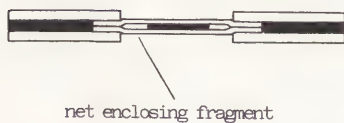


Figure 8 - cross-section of net window mount



Figure 9 - the complete mount



Figure 10 - a mount for four fragments

placing it between the boards as they were being stuck together, (fig. 5). The boards were cut together on the fretsaw, which can easily cut through two thicknesses of card at once.

For more three-dimensional textiles a thicker mount was necessary otherwise they would protrude and suffer pressure damage. Although two boards could be laminated together to form a deeper recess, and then be stuck to the back board together, the extra weight and slower cutting that resulted meant a lighter weight core was preferable.

A variation on the above mounting system was devised by laminating Plastazote polyethylene foam (11) of varying thicknesses varying from 3 mm to 12 mm between the two boards. This made an excellent supporting structure for objects such as felt knots and a hair braid. The materials have been tested and are preferable to commercially available foam core boards, the constituents of which are not always known, and which can be acidic and contain chlorides. A sheet of foam of the required thickness was therefore selected and cut to the same size as the board, and stuck to it using the same adhesive as before. This was then cut with the electric fretsaw and stuck down to a second piece of board as before (fig. 6). A window mount for thick pieces can be made in the same way by inserting a piece of Melinex between the foam and the second board, which necessitates cutting the whole 'sandwich' in one operation (fig. 7).

The mounting system is versatile and can be adapted in other ways to provide solutions to other problems. For example, a fragile piece can be sewn between net and mounted in the usual way, adhering the net between the boards for greater stability, as in the case of a knotted silk hairnet in this collection. A net window mount can be made by adhering net tautly to the cut-outs of both top and bottom boards, and then laminating these together with the textile sandwiched between the two layers of net (fig. 8).

After mounting, the boards or foam 'sandwich' were placed in a Melinex sleeve (12) already sealed along the two long sides, the dimensions of which allowed the boards to fit in snugly (fig. 9). For the foam boards and the double-size boards, correspondingly larger sizes of sleeves were available. This formed the primary housing for the textiles (fig. 10); approximately ten mounts were then stacked on top of each other and stored flat in strong drop-front boxes (13) lined with archival quality material (fig. 11).

#### Advantages of this method of mounting textiles

1. Flat storage of fragments with adequate support all around each one to minimize lateral movement.
2. Visibility without the necessity to undo or move any part of the package.
3. Buffered environment resistant to changes in relative humidity.
4. Protection against dust and light.
5. Accessibility - fragments are not stitched or stuck down in any way to the mount and can be removed if necessary for display, photography, etc.
6. Flexibility - the system can be adapted to allow viewing from the reverse, mounting thicker pieces by building up the support, and mounting fragile or fragmentary pieces between net.
7. Standardization of size - boards, Melinex sleeves and boxes can be ordered so that one fits into the other in a modular system.
8. Relatively low cost of materials used, which are readily available.
9. Use of non-toxic and stable materials.
10. Speed and ease of process.

#### Discussion

This method of mounting is unsuitable for light and flimsy textile fragments, e.g. wool threads, pieces of silk, small scraps. They are attracted to the Melinex sleeve by its static charge, and if this is moved for any reason, will adhere to it and not stay in the recessed cut-outs. This can be overcome by stapling a sheet





Figure 11 - storage of  
counts in boxes

of Melinex over the fragments using non-rusting staples, before slipping the boards into the sleeve. The possibility of Melinex attracting dust and shed fibre particles to itself could possibly be minimized by wiping it with an anti-static agent, but it is not known what effect this would have on the textiles. The use of an anti-static gun or any alternative transparent, chemically-stable, non-static covering material should be further investigated.

#### ACKNOWLEDGEMENTS

I would like to thank my colleagues at the Museum of London for many helpful discussions, particularly Frances Pritchard on the textiles, Tony Dyson and Mike Rhodes on the archaeology of the Baynards Castle dock and inn sites, and Nick Griffiths for the illustrations.

I gratefully acknowledge the help of the Museum of London, the Radcliffe Trust and the Friends of Fashion, whose funding made this mounting project possible. I am indebted to Poppy Singer, who originated many of the ideas for the conservation and mounting of these textiles, for her generous advice and helpful comments.

#### REFERENCES

1. Archaeology in the City of London - recent discoveries by the Department of Urban Archaeology, Museum of London (1980).
2. The treatments for these textiles varied from simple washing, then use of different lubricants, to ones similar to those used on waterlogged leather in the seventies. Iron salts were attacked by immersion in Detarex 100 (the tetra sodium salt of ethylene diamine tetra-acetic acid, pH 11.8 in 1% solution), followed by an acidic neutralising bath, rinsing in running water, and drying through acetone baths. Dressings included lanolin-based compounds and dilute leather dressings i.e. mixtures of oils, Bavon ABP or 520S and fungicides in solvents.
3. E. Crowfoot, F.A. Pritchard and K. Staniland, Medieval Finds from excavations in the City of London. Dress II: Textiles and clothing, London (forthcoming). F.A. Pritchard, 'Traces of vanished splendour - medieval textiles from London' Popular Archaeology, October (1985). J.L. Nevinson, 'Buttons and Button-holes in the fourteenth century', Costume 11 (1977) 38-44.
4. C.H. Brown, Structural Materials in Animals, Pitman, London, (1975). M.L. Ryder, Hair. Studies in Biology. Arnold, London (1972).
5. M. Delacorte, E.V. Sayre and N. Indictor, 'Lubrication of deteriorated wool', Studies in Conservation 16 (1971) 9-17.
6. S. Landi, The Textile Conservator's Manual, Butterworths, (1985). S.J. Wolf, 'Housings for Archaeological Textile fragments', Conservation Notes 12, Texas Memorial Museum (1985). L.V. Singer, 'The mounting of an embroidery onto fabric-covered Perspex', The Conservator 9 (1985) 22-25. D. Piechota, 'Storage containerization: archaeological textile collections', Journal of the American Institute of Conservation 18 (1978) 10-18.
7. Hercules Incorporated Klucel hydroxypropyl cellulose - Chemical and physical properties, manufacturers booklet (1981). J. Hofenk-de Graaf 'Hydroxypropyl cellulose, a multi-purpose conservation material', ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa 81/14/9 (1981).
8. 220 hours at 90,000 lux which induced fading up to Blue Wool standard No. 6, did not yellow a film of Klucel. Oven ageing at 50°C for nine months left film unaffected.
9. R. Howells and A. Burnstock, 'Polymer dispersions artificially aged', The Conservator 9 (1985) 46-47. Stockist: Vinyl Products Ltd., Mill Lane, Carshalton, Surrey, England SM5 2JU.
10. Melinex (U.S. Mylar), a range of clear polyester films based on polyethylene terephthalate obtainable in rolls, manufactured by ICI. Stockist: Polyester Converters Ltd., 1-27 Sumner Road, Peckham, London SE15.
11. Plastazote is a fine cell, low density polyethylene foam, sheet size 1500 x 1000 mm, thickness 3-27 mm, non-absorbent and chemically resistant. It has been tested by the British Museum who have been using it since 1977. Stockist: Wilford Polyformers

Ltd., Greaves Way, Stanbridge Road, Leighton Buzzard,  
Bedfordshire LU7 8UB, England.

12. Melinex sleeves are available in 50, 75 and 100 micron grades,  
any size. Stockist: Atlantis Paper Co. Ltd., Gulliver's Wharf,  
105 Wapping Lane, London E1 9RW.

13. Museum board and conservation binding boxes both stocked by  
Atlantis, see above.



## SUMMARY

A three year project into the special conservation problems associated with painted flags and banners is described. An outline of the treatments carried out is given. The conclusions reached from the work forms the main body of the paper, particularly in relation to cleaning, relaxation of distorted paint and sympathetic consolidation of both textile and paint elements.



Fig.1 Chinese Junk Flag, before conservation.  
Measurements:  
178 x 198 x 186cm



Fig.2 Blue Silk Flag, before conservation.  
Measurements:  
53 x 64cm

# THE TREATMENT OF PAINTED FLAGS AND BANNERS AT THE NATIONAL MARITIME MUSEUM, GREENWICH

N.T. Muir and N.S. Yates  
Textile Conservators  
National Maritime Museum  
Greenwich  
London SE10 9NF, England

## Introduction

In July 1983, at the 4th International Restorer Seminar held at Vezprem in Hungary, the particular conservation problems associated with painted flags and banners were fully discussed. A comparison was drawn between treatment of easel paintings and painted textiles, the latter inevitably falling between the two specialist fields of textile and easel paintings conservation.

The aims of the textile conservation section at the National Maritime Museum, as regards the treatment of painted flags and banners in the Museum's collection, were presented, and in this paper it is intended to bring developments up to date.

The trainee appointed in 1981 to work specifically on the painted flags and banners, Nicola Yates, has been working with both the textiles and the easel paintings conservators. Her experience on painted flags and banners arises mainly from work carried out on several flags for a special project as part of the NMM Diploma in Conservation. A questionnaire was also sent to textile conservators here and abroad to establish what techniques are currently in use. It is intended to publish the results in another paper (1).

The flags for the project were chosen to provide examples of different paint problems, as well as the common problem of textile/paint conservation, and although a very brief outline of their treatment is given here, the conclusions reached during the work on these flags form the main part of this paper.

The principal topics considered for the project were as follows:

- a) Consolidation of painted areas; which consolidant to use and when to apply them.
- b) Relaxation of distorted paint.
- c) Cleaning of a painted textile, with due regard to both the paint and the textile elements.
- d) Conservation of the textile elements in sympathy with the painted elements.
- e) Storage and display of painted flags.

The following 4 flags exhibited some of the problems required for these topics.

1. Russian Revolutionary flag c. 1919, painted on both sides, oil paint on wool; showed extreme flexibility differences between painted and non-painted areas; both fabric and paint had split badly in painted areas, and the paint was also very distorted. Measurements: 116cm x 167cm.

Treatment after full documentation and testing:

- Washing flat in detergent solution.
- Pinning out, weighting creased, painted areas with glass weights over Silicone release paper, and realignment of distorted areas while flag drying.
- Support of painted areas only onto a fine woven polyester Stabiltex sprayed with the ethylene vinyl acetate co-polymer adhesive, Beva 371, 1:3 in white spirit, heat-set in place.
- Any splits still tenting-up secured with small amount of neat Beva 371 from the right side.
- Whole flag stitched to dyed nylon net on the reverse.

2. Chinese Junk flag c.1842, (Fig.1) gum, oil paint and gilding on one side only of silk damask. Silk in sound condition, but gilding badly creased and cracked in most areas, also cupping quite badly, with some areas of loss. Measurements: 178cm x 198cm x 186cm

Treatment

- Surface cleaning of lacquered gilding unnecessary.
- Gilding consolidated using Beva 371 adhesive. Most effective results obtained by applying a 1:1 concentration of warmed adhesive solution in white spirit round edges of design with a fine brush, which prevented the 1:3 concentration applied to the central areas from spreading into the surrounding fabric. Process repeated on reverse.



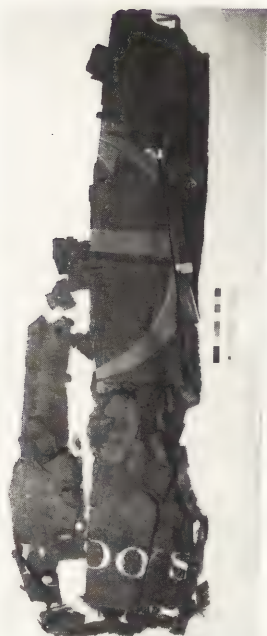
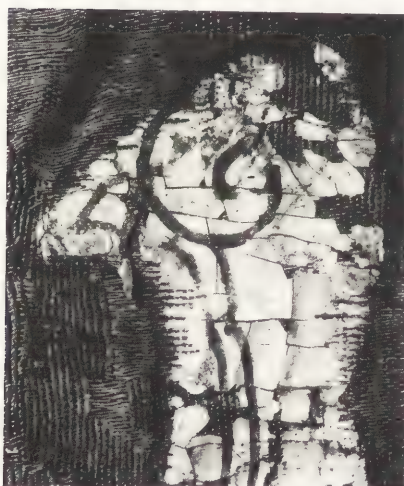


Fig. 3 Banner of Sir John Colpoys, before conservation. Measurements: 36cm x 173cm



Before consolidation



After consolidation with Beva 371.

Fig. 4 Detail of paint/leaf on Chinese Junk Flag, face view.

- Washing in a non-ionic detergent (Synperonic n) solution.
  - When drying, pinned out face up onto a polyester Melinex covered board, care taken to watch for cupping of gilding. Beva 371 proved an effective barrier to the moisture and no cupping occurred.
  - Excess adhesive removed from obverse surface with a swab lightly dampened with white spirit.
3. Blue silk flag, 19thC, (Fig.2) double sided, oil paint on silk. Paint secure on fine single layer of silk, but stiffness of paint had caused splits through both paint and fabric, with some fragments lost. Measurements: 53cm x 64cm

#### Treatment

- Painted motif supported from reverse onto dyed fine woven silk Crepeline, spray-coated with Beva 371 adhesive, 1:3 in white spirit.
- Some consolidation of green pigments only carried out using Beva 371, 1:4 in white spirit.
- Washing flat in detergent solution, followed by drying smoothed out onto Melinex.
- Whole flag sandwiched between dyed silk Crepeline and stitched.

4. Banner of Sir John Colpoys c.1800, (Fig.3) double sided, oil paint on cotton. Effectively a painting in that the whole textile area was painted on both sides. Very brittle, with numerous sharp, rigid creases, many of which had split creating fragments. Earlier repairs and restorations were causing damage. First requirement of treatment was to relax flag sufficiently to allow viewing, followed by support of entire flag. Measurements after humidification: 173cm x 180cm.

#### Treatment

- Humidity treatment in purpose-built 'chamber' to unfold flag.
- Removal of old patches and adhesive tape repairs.
- Distortions and unevenness removed by localised relaxation with pads of lightly dampened tissue weighted down.
- Larger splits edge-joined using acrylic-based emulsion, Lascaux adhesive 20X.
- Minor consolidation of flaking paint with Beva 371 adhesive 1:4 in petroleum spirit.
- Predyed polyester Stabiltex spray coated with Beva 371, 1:3 in petroleum spirit and heat set to reverse of flag.
- Supported banner fixed to covered board for storage/display.

#### Conclusions resulting from project

The work carried out on the project saw for the first time, in such depth, a serious attempt to draw and adapt techniques from both sides of textile and painting conservation. These have answered some of the problems, but it is evident that new techniques need to be developed to provide a sympathetic treatment for painted flags and banners.

One of the first problems often encountered with painted flags is the need to find a suitable consolidant for the painted areas to prevent further loss during subsequent treatments (ie. the consolidant unifying and strengthening the fragmented surface). It was found that a consolidant can have the additional function of isolating the damaged or water-soluble paint from water. If it is desirable to wash a flag, a number of consolidants could be considered for this purpose and adhesive tests were carried out, but many have the major disadvantage of being reversible only in solvents (such as IMS and acetone) that may also remove or undermine the paint. Other consolidants may form very glossy films or significantly stiffen the textiles.

It was found that Beva 371 having been specifically designed for use with paintings on canvas exhibited several useful characteristics such as its reversibility in white spirit, (definitely over short term, possibly less reversible in the long-term), its matte appearance (although slightly glossy when heat-set), good adhesion and flexibility. From our experience it also appears to form an effective barrier during washing, and if applied in low concentrations (below 1:4) little staining occurs. It may also be removed from the paint surface after washing, if required, with swabs dampened with white spirit. However, there are drawbacks that should be mentioned; in higher concentrations (above 1:4) staining and darkening may be visible and a slightly waxy feel discernible which could attract dust to the surface and should be taken into account when displaying the object. It can be toxic to the operator due to the toluene and petroleum spirit carriers;





before washing



after washing

Fig.5 Details of a symbol on Chinese Junk Flag, face view in raking light.



before paint distortions were treated.



after washing and treatment of paint distortions.

Fig.6 Detail of Painted Area on Russian Revolution-ary State Flag.

suitable ventilation is necessary when using it. It is reversible in toluene and other aromatic hydrocarbons, which must be considered when testing the paint, although it is questionable whether it would be desirable to remove any consolidant entirely at a later date. Unfortunately little independent research appears to have been carried out on the long term effects of Beva 371.

Although we would not advocate the use of Beva 371 as a consolidant in all cases, it appeared to work successfully on the Chinese Junk flag and Blue silk flag and allowed both flags to be washed without damage to the paint. (Fig.4) Of the current choice of consolidants, Beva 371 was the only adhesive that could have been safely used on these two flags but other consolidants have useful properties (eg. less staining, no waxy feel and less toxic) that could be utilised in different circumstances; eg. Hydroxy propyl cellulose, Klucel G may be of use when consolidating a powdering paint surface where areas of textile remain uncoated (providing the flag is not washed, as Klucel is water soluble at temperatures that are normally used for washing textiles) because very little staining occurs; it remains soluble in water and is non-toxic to the user. Where the paint is stable to solvents such as IMS and acetone other consolidants such as ethyl methacrylate (Paraloid B72) and polyvinyl butyral (Mowital B30H) may have more desirable properties. The questionnaire revealed that a number of people applied consolidants after washing, rather than before, which is hard to understand considering the high risk of paint loss due to flexing during the washing process, involving as it does, an inevitable amount of handling and stressing from the action of the water.

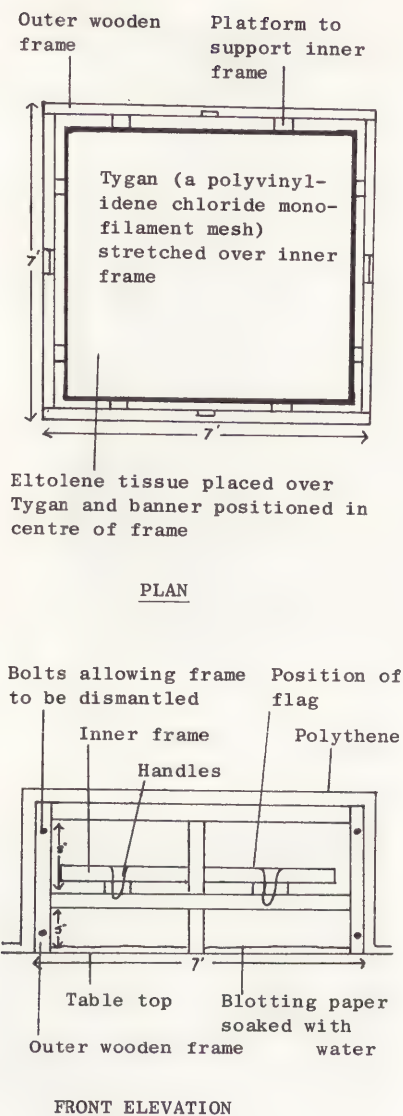
When considering how the textile and paint areas of flags should be cleaned, various alternatives may be considered, such as solvent cleaning of the textile with separate surface cleaning of paint. However, the dry-cleaning solvents commonly used, may dissolve or affect the paint media, so very careful testing is imperative. In general oil-based paints respond well to surface-cleaning techniques used by paintings conservators, providing the paint surface is well-bound, in relatively sound condition, and loose flakes are not lifted by the swabs (a low powered microscope is used for examination of the paint layers). Care must also be taken when surface-cleaning the paint that solvents do not drive dirt into the surrounding textile. A certain amount of dirt may also be removed by surface cleaning the textile with a soft brush although it is less effective than wet cleaning, but may be the only answer in some circumstances.

Although the washing process is regarded with apprehension by paintings conservators, it can be very beneficial to the textile support provided sufficient consideration is always given first to the effects it may have on the paint. Washing has been known to result in weakening adhesion of paints, break down of media, delamination and loss of flaking areas. This danger must be guarded against by isolating the paint from the washing water with a consolidant, as mentioned previously. The benefits of washing to the textile are well known, (with due regard to the possible loss of historical information), but very careful consideration of all points must be taken into account in each case before embarking on washing a painted flag. The paint and textile must be considered of equal importance when deciding upon a particular treatment.

After due consideration and careful testing, three of the painted flags included in the NMM project were successfully washed and the overall condition improved in each case. (Fig.5) Although the normal washing procedure for unpainted textiles was followed, a few precautions regarding the paint were observed, such as preventing any flexing or surface agitation of these areas and reducing to a minimum the length of time the object remained wet (although the flags were allowed to dry naturally). If a painted textile dries too quickly, edges of the paint may begin to curl.

Various methods may be used for holding the flag in position whilst drying; the most widely used technique involves pinning onto a polyester foil (Melinex) covered soft board and allowing the flag to dry naturally. This allows careful realignment of the weave and even drying, and the very smooth surface can help to enhance the natural sheen of silk fabrics. Small glass weights may also be positioned easily (over silicone release paper) at any stage to prevent distortions in the paint occurring during drying. Small silk flags may be smoothed onto fixed Melinex where the natural cohesion between the textile and surface helps hold the flag in position while it dries (glass would normally be used for this purpose with unpainted textiles but paint is likely to





All wood used in constructing the frame was varnished to prevent any uptake of moisture by it. If left unvarnished it would have been difficult to reach a very high humidity.

Fig.7 Wooden Frame Constructed to Form the Basic Support for the Humidity Tent for the Sir John Colpoys Banner.

stick to glass and should never be used). Both techniques were used successfully on the flags conserved for the NMM project.

Several methods were found to be effective in relaxing distorted paint. A secondary result of the washing process was the introduction of moisture to the object, enabling paint distortions to be flattened with glass plates over silicone release paper. This method worked particularly well on the 20th C. Russian Revolutionary flag. (Fig.6) Another variation on this method is the use of a humidity tent, allowing the introduction of controlled moisture which was particularly valuable in treating the double-sided banner of Sir John Colpoys which resembles a painting more than a flag. (Fig.7) The moisture successfully relaxed the embrittled, painted cotton for a short time, allowing the banner to be unfolded. Although successful in this case it is very dependent on the nature of the paint involved. Marion Mecklenburg (2) and Gerry Hedley (3) have carried out some very interesting experimental work into the moisture response of canvas paintings which relates very well to these problems. Relaxation of distortions, particularly cupping of paint flakes may be treated with the application of heat through silicone release paper from a spatula iron when heat-setting the consolidant. The relocation of the flakes may also be helped by the re-alignment of the weave after washing when the flag is pinned into its correct shape. This provides a similar treatment to that of pre-stretching used on paintings.

Other problems often encountered with painted flags involve splits through the painted areas (through paint and fabric). (Fig.8) Three of the flags used for the project represented many of the types of splitting commonly found in painted flags. In cases where the flag is either very weak (unable to withstand stitching), almost completely painted or the interface between the textile and paint is very weak and splitting, it may not be possible or desirable to stitch it to a support, therefore the flag will almost certainly have to be adhered to a fabric support. Conventional treatments involve the use of hand irons and vacuum hot table for applying the adhesive support fabric. (Fig.9) The hand iron can involve uneven application of heat which may affect the adhesive bond between the textile and the support fabric, but it is difficult to deal with any unevenness of the textile (particularly when brittle or multi-seamed textiles are involved) with the vacuum hot table or the cold table.

An adaptation of these commonly used adhesive techniques may be used on areas where splits only occur through painted areas, whereby a very fine support fabric (polyester Stabiltex or silk Crepeline) may be sprayed with a suitable adhesive and only applied to the painted areas on the reverse of the flag. (Fig.10) This provides a very useful method of holding the splitting areas in place and preventing them from creating tears into the surrounding textile. When dyed to a suitable colour the support fabrics are almost invisible. This method proved successful on the Russian and Blue silk flags in conjunction with the adhesive Beva 371, which was again chosen for similar reasons to those mentioned previously, but again we would not advocate its use in all cases. The spray application of the adhesive onto the support fabric gives very satisfactory results and testing quickly shows how much adhesive is required. (We have also had similar success spraying polyvinyl acetate co-polymer Vinnapas EPI diluted with water, particularly in conjunction with unpainted objects).

Where possible, it still appears to be preferable to use stitching techniques when applying an overall support, particularly to a double-sided banner. This is easily reversible at anytime, whereas adhesives are almost impossible to remove completely from a textile and therefore should only be used as a last resort. However, the combination of an adhesive support on the painted areas (from which it is more easily removed) with an overall stitched support on the textile (when required) can provide a successful treatment. Care must be taken when considering this method that the interface between the textile and paint is not particularly weak and that minimal additional stiffening of the paint occurs that may lead to splitting in this area, if flexed. Stitching around the painted areas, again, if the textile is not too weak, can help to provide additional support by closely attaching it to the overall support fabric. It also helps prevent movement of the support fabric over the paint surface which could lead to slight abrasion of the paint.

Such a wide variety of paints and pigments, and techniques of applying them to a wide range of fabrics, have been used in the production of painted flags and banners, that we must continue to



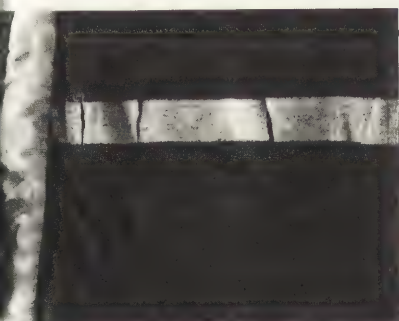


Fig.8 Splits Through Paint and Fabric on Russian Revolutionary Flag.



Fig.9 Verso of Russian Revolutionary Flag showing Polyester Stabiltex Heat Sealed to Painted Area and the Overall Nylon Net Support Stitched in Position. (Fig.8 shows same area before treatment).



Fig.10 Sir John Colpoys Banner after the Polyester Stabiltex has been Heat-Set to the Verso using a Hand Iron and then Stitched to a Covered Board.

develop a range of adaptable conservation treatments to cope with them. With this in mind, work is required in the possible use of facing techniques, as used by paintings conservators, for badly flaking paint surfaces, and the extended use of the hot and cold vacuum envelope and table systems and humidity treatments. The search for more suitable adhesives continues; types, methods of application, use as consolidants and means of attachment of support fabrics requires investigation. It is also hoped to try to determine more fully the effects of water on painted surfaces/coatings. Further research will also continue into the types of pigment, media and fabrics used in flag construction, their makers and histories.

#### References

1. N.S. Yates, "Results from a Questionnaire on the Conservation Treatment of Painted Flags and Banners" Preprints eighth Triennial Meeting of the International Council of Museums Committee for Conservation, Sydney, 1987.
2. M.F. Mecklenburg, "Some Aspects of the Mechanical Behaviour of Fabric-supported Paintings." Report to the Smithsonian Institution; Smithsonian Press, Washington, DC; Feb 1982.
3. G. Hedley, "The Moisture Response of Canvas Paintings" and "Why Paintings Shrink" papers presented at a UKIC Meeting on Lining and Moisture Based Treatments, Courtauld Institute, Nov. 1986.

#### Bibliography

- Berger, G.A. "Formulating Adhesives for the Conservation of Paintings. In Conservation and Restoration of Pictorial Art. Brommelle, N.S. & Smith, P. (Eds.) London. 169-181. 1967
- Berger, G.A. "Testing Adhesives for the Consolidation of Paintings." Studies in Conservation, 17. 173-194. 1972
- Thomsen, F.G. "An old Adhesive - Starch Paste. A New Technique. The Suction Table offers New Horizons in the Treatment of Brittle Textiles. Paris Congress Preprints 1984, 74-77.

#### Materials and Suppliers

Beva 371  
(Ethylene vinyl  
acetate adhesive)

Klucel G  
(Hydroxypropyl  
cellulose)

Melinex  
(Polyester film)

Stabiltex  
(Fine woven  
polyester)

Tygan  
(Monofilament  
screening)

Frank Joel Ltd.  
Unit 5  
Oldmedow road  
Hardwick Industrial Estate  
King's Lynn  
Norfolk. PE30 4HH

Hercules Ltd.  
20, Red Lion St.  
London WC1R 4PB

Boyden Data Papers Ltd.  
Trade Services Division  
Parkhouse street  
Camberwell  
London SE5

Swiss Silk Bolting Cloth Co. Ltd  
Grutlistrasse 68  
Postfach  
8027 Zurich 2  
Switzerland

Fothergill & Harvey Ltd.  
Industrial Textiles Division  
Summit  
Littleborough  
Lancs. OL15 9PQ





## SUMMARY

Burial-induced color changes in unmordanted and mordanted alizarin-dyed fabrics were studied and characterized. Cotton and wool samples were pre-mordanted with five common mordants (aluminum, copper, chromium, iron, and tin), dyed with alizarin, and buried in moist sandy loam soil at 28°C for one to six weeks. Periodically samples were removed from the soil, and the colors of the samples were measured in CIE color coordinates. Color differences between samples were measured to determine the effect of mordanting and burial on the shade and depth of shade of the alizarin-dyed cotton and wool fabrics. Analysis of metal ions present in the dyed samples was carried out using X-ray fluorescence to determine the degree of mordanting that had occurred and the effect of burial on the metal content of the fabric samples.

Burial of the mordanted and unmordanted dyed samples caused significant and progressive change in their shades and depths of shade. Chromium, copper, and iron mordanting was much more effective in preventing color change in the dyed cotton and wool samples during burial than aluminum and tin mordanting or no mordanting of the samples. Extensive metal exchange and uptake of iron was found in the buried samples.

## BURIAL-INDUCED COLOR CHANGES IN UNMORDANTED AND MORDANTED ALIZARIN-DYED COTTON AND WOOL FABRICS

Howard L. Needles  
Professor of Textile and Materials Science  
Marilyn E. Regazzi  
Graduate of Textiles M.S. Program  
University of California  
Davis, CA 95616

Introduction

Archaeological specimens of historic textiles found in burial sites are often exposed to the most severe conditions. Exposure to bacteria, yeast, algae, and fungi causes severe discoloration and degradation of dyed textiles (1,2). The dyed textiles change color on burial in damp soil with the nature and degree of color change affected by the fiber and dye type present in the textile, the presence of mordants on the textile, and the soil burial conditions encountered (2). Therefore, identification of the dyes and mordants present on buried archaeological textiles is made more difficult due to these changes in color.

In a recent study, we examined burial-induced color and shade changes in unmordanted madder-dyed cotton and wool fabrics and in fabrics premordanted with aluminum, copper, chromium, iron, and tin. The unmordanted and premordanted, madder-dyed cotton and wool fabrics underwent extensive color change during burial due to metal exchange. The metal ion exchange process was complex involving selective gain and loss of different metal ions. The fabrics recovered from the soil after burial therefore did not represent the color of the original samples, since ion exchange during burial had markedly changed the nature and distribution of metal-dye complexes present in the fabrics.

The nature of color change and metal exchange in madder-dyed fabrics is also complicated by the fact that madder contains a complex mixture of dyes including alizarin, purpurin, rubierythric acid, rubiatin, and munjistin (4). Alizarin is the dye present in the highest concentrations in madder, and synthetic alizarin entirely supplanted madder in production of Turkey red dye by 1886 because its color was more brilliant, had similar fastness and was less expensive (5).

In order to gain a better understanding of the nature of specific dye-mordant interactions and metal exchange processes during burial, cotton and wool samples premordanted with five mordants (Al, Cr, Cu, Fe, Sn) were dyed with alizarin. Unmordanted, alizarin-dyed samples were also prepared. Unmordanted and mordanted alizarin-dyed cotton and wool samples were buried in a moist sandy loam topsoil. Individual samples were removed at one, three, and six weeks. The colors ( $L^*$ ,  $a^*$ ,  $b^*$ ) of the samples before and following burial and color differences induced by mordanting and burial of the samples were measured. Changes in the metal contents due to mordanting and burial six weeks were measured using X-ray fluorescence.

Experimental

The fabrics used were an unbleached cotton muslin (80 x 80 picks/in., 5.2 g/m<sup>2</sup>) from Testfabrics, Inc., and a plain weave worsted wool (50 x 40 picks/in., 7.8 g/m<sup>2</sup>) from Burlington Industries. The five metal salts used as mordants were aluminum potassium sulfate (Al), potassium dichromate (Cr), cupric sulfate (Cu), ferrous sulfate (Fe), and stannic chloride (Sn). All were reagent grade. Reagent grade alizarin dye was also used.

Prewetted cotton and wool samples were premordanted in 1% aqueous metal salt solutions for 1 hr at 100°C. The samples were rinsed in distilled water, prior to dyeing. Mordanted and unmordanted fabric samples were dyed at 100°C using a liquor ratio of 100:1 for 1 hr in dyebaths containing 2% alizarin based on weight of fabric (owf). In addition, 20% (owf) sodium chloride and 5% sodium carbonate (owf) were added to cotton dyebaths and 20% (owf) sodium chloride and 2% (owf) sulfuric acid were added to wool dyebaths prior to dyeing of the fabrics.

Undyed cotton and wool fabrics and unmordanted and mordanted alizarin-dyed cotton and wool samples were buried in a moist, non-sterilized sandy loam topsoil according to AATCC Test Method 30-1981. Samples were removed at one, three, and six weeks, rinsed in distilled water, and dried prior to analysis.

Color measurements of the samples were made on a MacBeth M5-2000 Spectrophotometer using the CIELAB color difference system and illuminant C. Color in L\*, a\*, b\* color coordinates and color differences ( $\Delta E$ ) were measured for unmordanted vs. mordanted alizarin-dyed samples (Table I) and for buried vs. unburied samples (Table III). The differences in metal contents of unburied and buried samples were measured on a Kevex 0700 Si-Li X-ray fluorescence spectrometer (Tables II, IV).

### Results and Discussion

Unmordanted and mordanted cotton and wool fabrics were successfully dyed with alizarin from light to medium shades (Table I). The unmordanted and mordanted wool samples tended to dye to much lighter shades than the cotton samples by this technique. Only chrome-mordanted wool dyed to a significantly deeper shade than the corresponding chrome-mordanted cotton sample. With exception of copper-mordanted cotton, mordanted cotton samples dyed to lighter shades and to much different shades than unmordanted dyed cotton with aluminum and tin-mordanted cotton samples having the greatest color differences compared to unmordanted dyed cotton. Mordanted, dyed wool samples were nearly the same shade or darker and a much different shade than unmordanted, alizarin-dyed wool with chromium, copper, and iron-mordanted dyed samples having the greatest color differences compared to unmordanted dyed wool.

Examination of the metal contents of unmordanted dyed fabrics compared to mordanted dyed fabrics showed the relative effectiveness of the premordanting process. Wool tended to retain much greater amounts of mordants than cotton on dyeing with alizarin, with premordanted wool retaining high levels of chromium and copper mordants, intermediate levels of iron and lesser amounts of aluminum and tin on dyeing. Cotton retained moderate amounts of copper, small amounts of chromium and iron after dyeing, while little or no aluminum and tin was retained in cotton samples premordanted with these ions.

On burial the unmordanted and mordanted cotton and wool samples underwent significant color and shade change with unmordanted and mordanted dyed wool samples showing much greater changes than the cotton samples (Table III). While unmordanted/undyed cotton underwent slight darkening and staining, unmordanted/undyed wool became progressively much darker and orange.

Unmordanted dyed cotton on burial became lighter and much more orange in character, while unmordanted/undyed wool samples darkened and became much more yellow. The mordanted dyed cotton samples tended to change little or become somewhat lighter in shade and became more blue in character. The observed color changes tended to become progressively greater with increasing burial time from one to six weeks.

The mordanted dyed wool samples underwent rapid color change on burial with the greatest changes occurring after one week of burial. Chromium and copper-mordanted dyed samples underwent the least color change during burial, while unmordanted dyed and aluminum, iron, and tin-mordanted dyed wool samples underwent much greater color change. All samples except chromium and copper-mordanted dyed wool became more purple in character during burial.

The sandy loam used in the study had high concentrations of iron and silicon. Small amounts of aluminum, chromium, and copper were present in the soil, and no tin was detected. Other heavy metal ions also were present in significant amounts.

The unmordanted and mordanted dyed samples underwent extensive changes in metal content during burial for six weeks (Table IV). All samples showed small to large uptakes of iron, the metal most abundant in the soil. Most samples took up aluminum in small amounts. In addition, all samples picked up small quantities of calcium, manganese, titanium, and zinc and moderate amounts of silicon from the soil during burial. These changes in the metal content of the burial samples demonstrate that extensive metal ion exchange occurred in the samples during burial causing extensive color change.

The findings for the alizarin-dyed samples in this study differed significantly from our earlier study of madder-dyed cotton and wool (3). The presence of a dye mixture on the fabrics as with madder has a profound effect on the type and distribution of dye-metal complexes formed on mordanting and burial of cotton and wool and the color changes observed.



### Conclusions

Unmordanted and premordanted alizarin-dyed cotton and wool fabrics undergo extensive color change during burial due to metal exchange with metal ions in the soil. The metal ion exchange process is complex involving selective gain and loss of different metal ions. The fabrics recovered from the soil after burial therefore do not represent the color of the original samples, since ion exchange during burial has markedly changed the nature and distribution of metal-dye complexes present in the fabrics. Therefore, identification of mordant-dye combinations used on dyed archeological textile recovered from moist burial sites is not possible in most instances, although the dye or dyes present on the textile can still be identified by chromatographic techniques. Observed color changes in unmordanted and mordanted alizarin-dyed cotton and wool samples do not correlate with changes in madder-dyed samples although alizarin is the major dye component contained in madder.

### References

1. Nopitsch, W., *Ciba Review*, **100**, 3578 (1953).
2. Needles, H. L., V. Cassman, and M. J. Collins, *Advances in Chemistry*, **212**, 199 (1986).
3. Needles, H. L. and M. E. Regazzi, *Preprints*, 15th Annual Meeting of the American Institute for Conservation, In Press.
4. Diehl, J., "Natural Dyestuffs" in *Textile Conservation*, J. Leene, ed., Smithsonian Institution, Washington, DC, 1972.
5. Hummel, J. J., *The Dyeing of Textile Fabrics*, 2nd Ed., Cassell and Co., London, 1886.

Table I

Color and Color Differences in Unmordanted and Mordanted Alizarin-Dyed Cotton and Wool Fabrics

Mordant	Cotton				Wool			
	L*	a*	b*	$\Delta E$	L*	a*	b*	$\Delta E$
None	43.6	10.0	-5.8	--	75.2	11.6	59.3	--
Al	80.1	13.8	12.4	41.0	80.4	8.0	61.2	7.9
Cr	59.8	22.4	2.3	22.0	25.5	23.2	15.5	67.6
Cu	30.5	15.7	-5.8	13.3	48.8	15.7	27.2	40.5
Fe	59.2	5.4	3.5	18.7	77.6	9.4	60.0	30.7
Sn	88.8	1.2	14.9	50.5	79.0	10.5	59.1	5.5

Table II

Differences between the Metal Contents of Unmordanted and Mordanted Alizarin-Dyed Cotton and Wool Fabrics

Mordant	Differences in Metal Contents									
	Cotton					Wool				
	Al	Cr	Cu	Fe	Sn	Al	Cr	Cu	Fe	Sn
Al	0.0	0.0	-3.6	-0.6	0.0	3.5	0.2	-0.3	0.2	0.0
Cr	0.1	20.1	-3.0	0.9	0.0	0.0	389.5	-0.7	0.1	0.0
Cu	0.0	0.1	136.5	0.5	0.0	0.0	0.0	430.2	-0.9	0.0
Fe	0.0	0.0	-1.5	50.3	0.0	0.2	0.1	-0.8	147.3	0.0
Sn	0.3	0.1	-3.8	-0.1	0.4	-0.2	0.0	-0.7	-0.3	12.3

Table III

Burial-Induced Shade and Color Differences in Unmordanted and Mordanted Cotton and Wool Fabrics

Mordant	Burial Time (weeks)	Cotton Shade Differences				Wool Shade Differences			
		$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta E$	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta E$
Undyed	1	-2.1	0.9	0.3	2.3	-9.7	4.5	7.4	13.1
"	3	-3.7	0.8	0.5	3.8	-11.2	3.6	7.8	14.1
"	6	-4.0	0.9	0.7	4.2	-16.6	3.4	2.2	17.4
None	1	6.8	3.7	4.9	9.1	-18.0	4.0	13.0	22.5
"	3	11.6	8.4	9.3	17.1	-28.4	6.8	55.4	62.6
"	6	13.9	3.2	10.5	17.7	-26.3	6.8	51.0	57.7
Al	1	-3.6	-3.4	1.4	5.1	-46.1	21.0	-36.0	62.1
"	3	-2.9	-2.4	-0.4	3.8	-28.5	16.2	-46.1	56.6
"	6	-4.9	-5.4	-2.2	7.6	-25.9	6.2	-45.3	52.5
Cr	1	0.5	-2.3	2.8	3.6	-2.4	-1.1	-3.7	4.5
"	3	0.8	-1.5	0.6	1.8	-3.1	-1.3	-5.4	6.4
"	6	2.0	-1.5	3.7	1.1	-2.7	-1.5	-5.3	6.1
Cu	1	3.1	-0.6	-4.5	5.5	14.7	0.5	3.1	15.0
"	3	-0.1	-0.5	5.5	5.6	-8.0	2.2	23.7	25.1
"	6	-5.0	-0.6	3.5	6.2	-5.4	1.7	21.8	22.5
Fe	1	-0.8	2.0	-1.9	2.9	-22.8	8.2	-35.3	42.8
"	3	2.8	1.8	-3.5	4.8	-24.8	11.9	-44.8	52.6
"	6	7.6	-0.4	-3.9	8.5	-24.9	10.7	-43.3	51.1
Sn	1	-7.4	2.0	1.7	7.9	-15.6	3.8	-26.6	31.1
"	3	-6.2	1.5	0.5	6.3	-24.4	15.4	-42.6	51.5
"	6	-9.1	1.0	-1.3	9.3	-30.2	8.2	-46.5	56.0

Table IV

Differences in the Metal Contents of Unburied and Buried Alizarin-Dyed Cotton and Wool Fabrics

Mordant	Changes in Metal Contents									
	Cotton					Wool				
	Al	Cr	Cu	Fe	Sn	Al	Cr	Cu	Fe	Sn
Undyed	3.7	-0.1	0.4	20.0	0.0	8.0	0.2	1.1	141.8	0.0
None	10.2	0.0	-1.3	176.6	0.0	5.0	0.1	2.8	62.5	0.0
Al	11.0	0.3	1.1	124.6	0.0	2.8	-0.1	2.1	32.8	0.0
Cr	6.1	2.0	0.4	44.3	0.0	1.7	22.1	1.7	13.8	0.0
Cu	5.1	0.2	-120.3	104.0	0.0	1.5	0.1	-226.5	64.4	0.0
Fe	13.2	0.1	0.1	124.1	0.0	1.3	0.0	1.8	10.5	0.0
Sn	7.7	0.1	1.8	84.4	0.0	3.9	0.0	1.7	65.9	2.5



## SUMMARY

The conservation for study and storage of two dissimilar collections of archaeological textiles initiated an investigation of mounting systems for two-dimensional textiles. A two-phase modular solution based upon standard sizes is described. It consists of a simple, ready-made temporary mount and a double-window mount for study and permanent storage. The modular format and standard sizes enables mounts to be constructed systematically and several at a time reducing both material waste and labour outlay without compromising material, design, or construction quality.

## ANTHROPOLOGICAL TEXTILES: A MOUNTING SOLUTION

E.E. Peacock  
Archaeology Department  
The University of Trondheim Museum  
Erling Skakkes gt. 47b  
N7000 Trondheim  
NORWAY

## INTRODUCTION

Numerous mounting systems have been proposed for the storage of collections of anthropological and historic two-dimensional textiles.<sup>1</sup> These systems have been designed to meet the specific requirements of particular collections and often are versatile enough to be adaptable to the needs of other collections. Mounts are custom made - after a system - to meet the needs of each textile specimen. That which is common to these systems is a high cost in materials and labour. Both factors make such systems prohibitively expensive for many institutions to consider. In addition, these mounts are often too elaborate for textiles requiring a short-term or 'basic' packaging solution.

It is understood that anthropological textiles require more customised packaging for storage than many other materials. Archaeological conservation laboratories which must address the seasonal influx of large numbers of freshly-excavated finds often have neither the material nor labour resources to adopt custom-made systems. There has long been the need for solutions which bridge the gap between the costly, more elaborate systems and making do with no system.

The present work describes a two-phase solution developed to satisfy the requirements of the two-dimensional textiles in two dissimilar collections of archaeological textiles. The system is not revolutionary; rather, it is the product of suggestions of and reported systems worked out by textile conservators adapted to a mass treatment strategy employing a modular format and standard measurements.

## BACKGROUND

The Svalbard Textile Conservation Project (1982-86) prompted an investigation of various storage systems suitable for conserved two-dimensional textiles which are too fragile to be handled but must be accessible for study and analysis. The project itself addressed the conservation of all textile finds recovered from the Nordic archaeological expeditions to arctic Svalbard (Spitsbergen) (1955-60) deposited to the Tromsø Museum, Norway. The scope of the project was to rescue the finds from the then storage conditions and, by pursuing a policy of minimal intervention, prepare them for accessible academic research and stable storage. Since excavation nearly thirty years ago the textiles had been neither examined by archaeologists or textile specialists nor conserved. Some of the collection has not been accessioned.

The collection includes over 350 fragments and larger pieces of bedding, clothing, and footwear constructed of woven, knitted, braided, felted, and looped needle netted (nålbunnet) wool. Although the expeditions investigated several localities along the west coast of West Spitsbergen, most of the collection was recovered at Russekeilla, an 18th century Russian hunting station. It is not yet determined where this collection will be permanently stored.

The other collection requiring a mounting solution consists of the textiles recovered from on-going, large-scale excavations of the mediaeval cultural levels in the city of Trondheim, Norway. This growing collection contains several thousand items, the majority of which are two-dimensional. The collection is stored in the climate controlled stores of the University of Trondheim Museum.

Both collections are study collections; the textiles are not conserved to exhibition standard. They require a storage/packaging system which: 1) is chemically stable, non-reactive and provides physical support to the textile; 2) leaves as much of the textile to view as possible; and 3) protects the textile from possible mechanical damage and chemical contamination from handling during the research process. A labour-intensive, custom-made storage container, be it a box, folder, or mount, for each textile cannot be considered.

## DESCRIPTION

A two-phase modular mounting system was selected. The two phases represent two levels of packaging and both satisfy the criteria outlined above. The first phase is based upon the resealable ('zip-lock') polyethylene bag. Although unsophisticated, it provides a simple, ready-made working mount for textiles in transition, e.g. awaiting conservation, just conserved.

Storage conditions following excavation or collection of anthropological textiles often accelerate deterioration. Frequently, when textiles are recovered from archaeological contexts, especially terrestrially wet or frozen burial environments, documentation prior to conservation is limited. Consequently, a textile may be subjected to considerable handling prior to and following conservation and before it reaches the stage of packaging for study and permanent storage. Other textiles which are not prioritised for conservation treatment also require immediate suitable packaging whether or not they will be conserved or remounted at a later date. The mount will not prevent further chemical deterioration of the unconserved textile but it does offer favorable protection.

The second phase is a double-window mount for study and storage. It consists of two lined window mats in an unsealed clear polyester film envelope (Fig.1). For thicker textiles the space between the two lined window mats is built up with layers of unlined window mats.

This phase is based on the mounting systems introduced by McLean and Pritchard.<sup>1</sup> The major difference between this and other systems is its mass treatment strategy. With other systems the mount is custom made to meet the requirements of each textile; with this system, the textile is placed in the appropriate size standard mount which is then customised to the needs of that textile. The modular format and use of standard dimensions also facilitate placement in standard size container systems used in storage.

Mounts are constructed in a range of sizes. The selected dimensions are standard measurements used in the paper industry in Europe, namely, the A system (A1 - A5). These dimensions provide a selection of mount sizes which are modular. This enables mats to be pre-cut and lined in batches. The basic mount is prepared independent of the textile to be mounted and several at a time. Using the standard dimensions of the A or similar system reduces material waste.

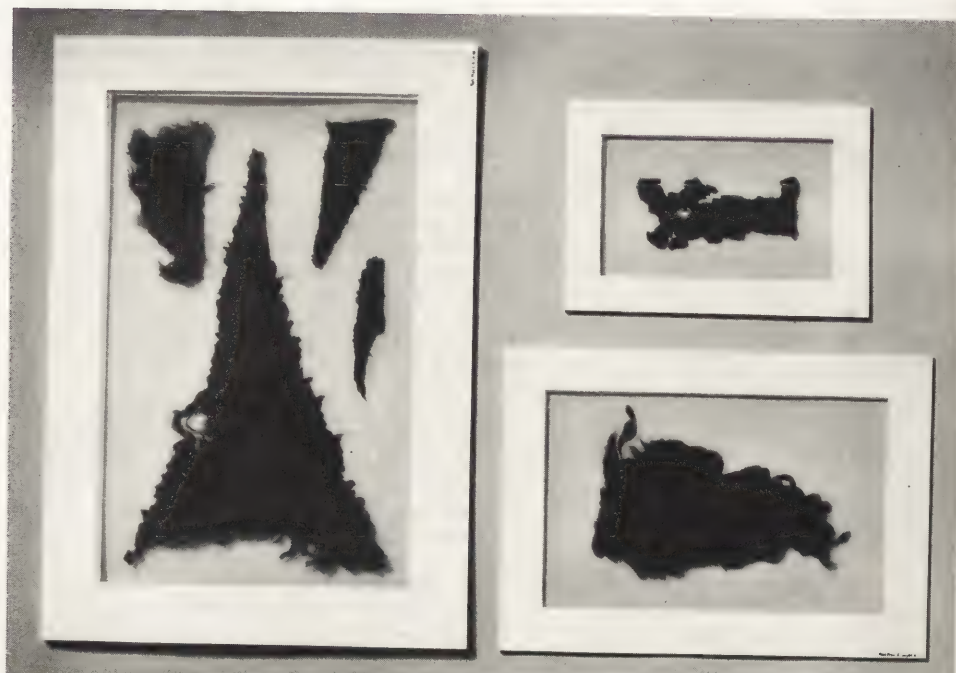


Fig.1 Double-window mounts lined with undyed silk crepe.  
(Photo: P.E. Fredriksen.)



## DISCUSSION

Prototype mounts were constructed and evaluated for use with both the Svalbard and Trondheim textile collections. Both fabric-lined and polyester film-lined mats provide successful double-window mounts. The different qualities of these lining materials must be considered when selecting the appropriate material for the mounting project at hand. Sheer lining fabric enables an exchange of air for the enclosed textile and the friction contact of its weave and nap with the enclosed textile fragment assists in holding the textile in place within the mount. Disadvantages of a lining fabric are: its lack of total transparency; its flexibility which may allow too much flexing of the fragile textile; and its chemical composition (not non-reactive) which may lead to degradation of the textile specimen over time.

The clear polyester film lining provides excellent viewing qualities. It is chemically non-reactive and its rigidity reduces flexing and abrasion of the textile fragment. Drawbacks to the film are: its degree of static charge which lifts off loose and deteriorated fibres and deposits them at random within the mount; the difficulty in securing the textile from sliding around in the mount; and the possible formation of an unfavourable micro-environment within a mount constructed of two polyester film-lined mats.

## PREPARATION

### Working Mount

The ready-made working mount consists of perforated resealable ('zip-lock') polyethylene bags in an assortment of standard sizes. Acid-free museum quality mat board (1.6 or 2.7 mm)<sup>2</sup> is cut to fit the bags loosely. The textile is placed upon an acid-free tissue lined board, slipped into the appropriate size bag and sealed. For larger pieces standard size bags can be made by heat sealing perforated tube or sheet polyethylene. All materials can be pre-cut in batches providing quickly-assembled working mounts when needed.

### Double-Window Mount

Cutting. Mats are cut out of acid-free museum quality mat board. Such board is available in a range of thicknesses. It is found that two thicknesses, 1.6 and 2.7 mm<sup>2</sup>, accommodate mounting needs. The mats are cut in standard sizes. The exterior dimensions employed are the standard measurements of the A system (A1- A5). The dimensions of the mat window are also standard (Fig.2). The front and back windows, as well as any internal layers, are cut the same size. The window of the outside mats may be cut bevelled; whereas, the window of the layering mats is cut at a right angle.

### STANDARD SIZES

FORMAT	MAT DIMENSIONS	OUTER BORDER
A5	14.8 X 21.0 cm	2.5 cm
A4	21.0 X 29.7	3.0
A3	29.7 X 42.0	4.0
A2	42.0 X 59.4	5.0
A1	59.4 X 84.0	7.0

Fig.2 Suggested range of mount sizes.

Each cut-out window can be recut to provide a smaller size mat. For example, the museum board required to supply one A1 mat will also supply one A2, one A3, one A4, and one A5 or combinations thereof. The A2 is cut from the cut-out window of the A1; the A3 is cut from the cut-out window of the A2 and so forth. The bevelled edges of each cut-out window are first recut to a right angle.

The thickness of museum board selected and the number and thickness of layering mats used must be judged based upon the overall size of the mount and the thickness of the textile piece(s) to be mounted. Several fragments of the same thickness can be placed in one mount; however, fragments of several thicknesses are not placed together in one mount. With larger mounts, e.g., A2 and A1, attention must be paid that the mats are thick enough to provide stability and not be subjected to warping.<sup>3</sup>

**Lining.** The front and back mat windows are lined with either sheer fabric or clear polyester film. Suggested sheer fabrics are silk and polyester organdie (Crepeline) and polyester multifilament (Stabiltex). Off-white, natural, and dyed varieties are suitable. Dyed varieties in pale earth tones complement anthropological textiles. Fabrics should be prewashed to remove residual materials from processing.

The mats are lined several at a time. Mats of one or various sizes are set out face down (with 4-5 cm spacing) on a free-standing flat, rectangular workspace, edges parallel to the edges of the workspace.<sup>4</sup> The lining fabric is stretched over the mats, weaving parallel to the edges of the workspace, and firmly secured under tension with tape along all edges of the workspace. Diluted polyvinylacetate emulsion is brushed through the fabric onto all edges of the mats. No weighting is necessary. When dry the mats can be roughly cut out from the piece of fabric and excess trimmed with a mat knife.

The other lining material is a 100% clear synthetic polyester resin film based on polyethylene terephthalate (Mylar, Melinex, Scotchpar). It is a strong, tough, dimensionally stable film available in a range of thicknesses from 0.25 - 14 mils. Appropriate types are entirely free of plasticisers, U.V. inhibitors, coloured dyes, impregnants, and surface coatings.

The thinner thicknesses of polyester film can be adhered to the window mat with polyvinylacetate emulsion. No pretreatment or lining up of the polyester film is necessary; the mat is simply adhered, under weight, face up onto the film. Several mats can be adhered simultaneously onto a large piece of film. The mats are roughly cut out of the film and excess film trimmed with a mat knife. Thicker films are adhered using a double-sided, transparent, pressure-sensitive tape (3M #415) consisting of an acrylic resin coated on both sides of a 0.5 mil polyester film.

**Assembly.** Layering mats are adhered to outside lined mats with polyvinylacetate emulsion or double-sided transparent polyester tape. Weighting is necessary with the emulsion. Several mats of the same size can be adhered, placed one atop another and topped with a weighted sturdy wood template of slightly larger dimensions than the window mat.

The textile fragment(s) are arranged on the inside of one lined mat. The two completed exterior mats can be joined together with: 1) gummed linen tape; 2) double-sided transparent polyester tape; 3) polyvinylacetate emulsion; or 4) a three-sided plastic list which is slipped over the edges on two or four sides. The method of joining is selected based upon the materials available, the dimensions and thickness of the mount, and the anticipated need for direct, hands-on access to the textile.

**Securing.** Textile fragments placed in mounts consisting of two fabric-lined exterior mats need to be secured to avoid shifting. It is found that intermittent tacking with silk (proteinaceous textiles)/cotton (cellulosic textiles) thread around the perimeter of the textile provides the necessary securing. Some authors recommend sewing either continuously around or through the specimen.<sup>1</sup> Regardless of method, the stitching must never be so tight that threads or the textile become distorted. In some cases, with small, thin textiles, the naps of both the silk lining fabric and the textile are sufficient to keep the textile in place and no sewing is necessary. Polyester lining fabric has less surface nap than silk.

Textile fragments will slide and bunch when mounted in a two-window mount constructed of one or more polyester film-lined mats. Sewing through the textile to the fabric lining is suggested for mounts consisting of one polyester film-lined mat and one fabric-lined mat. Securing fragments in mounts constructed of two polyester film-lined mats is noted as time consuming. Both Wolf and Gardner<sup>1</sup> describe securing textile fragments to polyester film with stitching. Stitching holes are made in the film prior to sewing and the ends of the sewing threads are fastened to the film with dots of polyvinylacetate. The sewing is carried out prior to joining the mats together.

**Protective Envelopes.** Each completed mount is placed in a protective envelope of clear polyester film. Envelopes can be purchased ready made or constructed in standard sizes of polyester film obtainable in sheets and rolls. The dimensions of the envelopes must exceed those of the corresponding mount to be protected. If purchased envelopes are used, the standard



measurements of the double-window mounts may have to be altered. The envelope is constructed by heat sealing (thinner thicknesses) or adhering with double-sided transparent polyester tape (thicker thicknesses) three of the four edges.

#### CONCLUSION

The packaging of two-dimensional anthropological textiles continues to be a challenge for conservators. The recent growing interest in the field of archaeological textiles has resulted in many suggested solutions. These systems commonly have a high cost in materials and labour. A two-phase modular solution provides a simple, ready-made working mount which protects the textile until it is prepared for permanent storage and a double-window permanent mount for study and storage. The modular format and use of standard dimensions is an efficient, cost-effective solution to a problem that has generally been resolved on a one-on-one basis previously. Labour and material costs are reduced without compromising material, design, or construction quality.

#### REFERENCES AND NOTES

- 1 Frame, Mary. Conservation techniques - conservation of archaeological textiles, *Textile Conservation News* (Sept 1980) 6-7; Gardner, Joan S. Pre-Columbian textile fragments from Ecuador: conservation procedures and preliminary study, *Technology and Conservation* 1 (1979) 24-30; McLean, Catherine C. Mounting small fragile textiles to be viewed from both sides, *Art Conservation Training Programs Conference, 1980, National Technical Information Service, Commerce* (1980) 77-83; Meikle, Marg. *Textile Conservation News* (Sept 1982) 5; Piechota, Dennis. Storage containerization: archaeological textile collection, *Journal of the American Institute for Conservation* 18 (1978) 10-18; Preservation Office Research Services, *Polyester Film Encapsulation*, Library of Congress, Washington, 1980; Pritchard, Frances. Personal communication, The Museum of London; Segal, Martha and Jan Vuori. The padded free mount, *Textile Conservation News* (Spring 1985) 21; Vuori, Jan. A method for putting crepeline onto mats, *Textile Conservation News* (Fall 1984) 11-14; Wolf, Sara J. Housings for archaeological textile fragments, *Conservation Notes* 12 (April 1985).
- 2 These correspond to 4-ply and 6-ply respectively.
- 3 It is found that the double-window A1 mount is not stable enough for thicker textiles. In these cases, a single-window mount is used. The lined window mat is prepared as described. The windowless mat is lined with a prewashed, unbleached linen-cotton blend fabric adhered around the edges.
- 4 If it is desired to have one mat of a fabric-lined mount lined on the bias to avoid the moiré effect, the mats are simply laid out with edges at a 45° angle to those of the workspace.





CONSERVATION OF THE CANVAS-WORK UPHOLSTERY OF TWELVE ARM-CHAIRS, THE WORK OF ANDREA BRUSTOLON, IN THE CA'REZZONICO, VENICE.

Francesco Pertegato  
Via Lanzo  
16-20123 Milano  
Italy

The twelve monumental chairs, padded and covered with decorative canvas-work panels, form part of the so-called "fornimento Venier" (Venier furnishings), one of the most sumptuous sets of 18th century Venetian carved wooden furniture. Produced for Pietro Venier di San Vio<sup>1</sup>, it probably dates to the first quarter of the 18th century<sup>2</sup>.

When Maria Venier married Alvise II Contarini in 1758, the entire group was transferred from Palazzo Venier to Palazzo Contarini degli Scignini; upon the death in 1838 of their last direct heir, count Girolamo, the set was left to the city of Venice. This legacy was initially kept at the Accademia di Belle Arti, but in 1900 the furniture was transferred to the Correr Museum and subsequently to the Ca' Rezzonico when this palace became the Museo del '700 Veneziano (Museum of 18th century Venice).

The chairs themselves (principally used for ceremonial occasions) are outstanding example of 18th century decorative carved woodwork (fig. 1). Their legs, arms and sides are carved in boxwood to resemble contorted tree-trunks wound around with tendrils and vine-leaves; negro figures extend up from the upper part of the front legs to support the arms; resting casually on the arm-rests near the back of the chair are nude putti. All the uncovered parts of the figures' bodies are in ebony.

Description of the Upholstery

The decorative design of the upholstery follows a scheme used extensively during the first half of the 18th century<sup>3</sup>: naturalistic or fantastic landscape containing symbolic animals and human figures are surrounded by wide borders consisting of mixtilinear geometric forms and garlands of stylized flowers. This upholstery has been frequently assumed to be produced according to the tapestry technique, but in fact all the pieces are embroidered in wool and silk on a dyed linen canvas. The embroidery is comprised of cross-stitch in coloured wool for the centre scenes; silk worked in a technique similar to satin stitch, using very short stitches and very twisted thread, specifically employed for the faces, arms and legs of the figures so as to obtain a more precise definition of features and variation in tone.



Figure 1



Figure 3



Figure 4



Figure 5



Figure 6

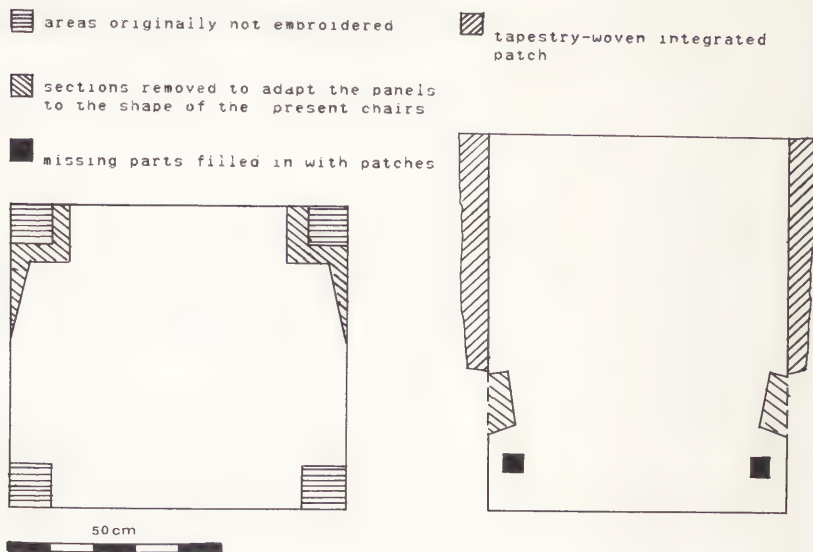


Figure 2

Notwithstanding their unusual compositional elegance, the variety of colours employed and the attention to detail – or perhaps due precisely to these characteristics – the upholstery would not appear to have been produced specifically for the Brustolon furniture, but to have been taken from a set of earlier furnishings. An indication of this is the fact that the panels used to cover the backs of the chairs have two 4 cm-square pieces cut out of them, their borders folded back and sewn down to the reverse; their position and size indicate that these openings corresponded to a differently-shaped arm-chair, for which they were probably originally created.

These openings were filled with patches which came from the cutting out of pieces to accommodate the arms of the subsequent (i.e. Brustolon) chairs, and from the redundant parts of the seat-covers.

This hypothesis for a re-use of the covers would seem to be confirmed by the fact that some rather crudely-worked tapestry fragments were incorporated into the sides of the chairs, whilst the linen linings were in part taken from the original dust-covers: they include a double row of button-holes which serve (with the help of a tape) to close them behind, plus a mark comprising a series of letters which served to distinguish between each of the chairs and its cover (this mark appears also on the padding of the chair-backs). During the course of conservation these patches were removed from the chair-backs and replaced in their original positions, thus enabling the standard form of the panels as they left the embroiderer's workshop to be reconstructed (fig.2). From this exercise it was clear that the chairs for which the covers were initially used were squarer in shape.

#### State of Conservation

All the panels were notably shorter along one diagonal than the other. This effect was undoubtedly due to the tension produced by the petit-point stitch covering the canvas, an effect also probably accentuated by subsequent washing.

Although the decorative scheme of the upholstery has remained substantially intact, a considerable proportion of the original materials used had been lost. More delicate and therefore vulnerable to abrasion, in many areas the silk had been lost, thus exposing the underlying canvas to further decay not only in the areas subject to wear and tear but also in those parts where wrinkles had formed because the padding no longer provided a sufficient support. In some areas, where the loss of support was most extensive, small tears had resulted in the canvas itself. In the areas most subject to wear and tear, for example in the upper border of the chair-back and that on the front of the chair-seat, areas of wool had been lost. A certain amount had also been lost due to the activity of insects (the clothes-moth), most noticeable in those areas corresponding to the parts where braid had been attached to the upholstery by means of a vegetable glue.

Where the canvas remained exposed it was possible to see the outlines of the original preparatory drawing, sketched in a grey-black ink.

Once detached from their chairs, the state of the upholstery became more clearly apparent: extremely stiff, dust-ridden and full of greasy and grimy dirt. The dust and dirt had darkened and dimmed the colours of the embroidery, already faded anyway as was evident from a comparison with those areas which had not been exposed to the light – and especially the wrong side of the panels. The metal tacks used to attach the upholstery to the wooden structure had produced a series of holes which had consequently weakened the edges of the panels. Also visible were the remains of two different glues, one used to attach an earlier



set of braid to the chairs, the other from some relatively recent repair-work.

#### Conservation Treatment

##### 1. Cleaning

Having vacuumed-cleaned the panels, it became evident that only by washing them in a water + detergent solution would the dirt and dust be removed and thus render the decorative design more clearly visible.

Preliminary tests as to colour stability and dimensional changes confirmed that washing would have no negative effect on them. A problem lay in the stability of the ink used for the preparatory drawings, however. Observed under a microscope this ink appeared to consist of a series of tiny particles whose adhesion to the textile fibres did not appear to be very strong. A further test was therefore necessary and this revealed that if the areas where the ink remained were not subject to rubbing or other mechanical stress, the ink remained stable.

Having removed the tapestry-worked integrated parts, the patches, the remnants of braid and the deposits of glue, the panels were prepared for immersion in detergent solution. Bearing in mind the necessity to retain the traces of drawing where they remained, washing was considered important to recover as much of the original aesthetic qualities of the panels as possible.

In addition to the normal procedure followed in washing the textiles, it was also found necessary to subject them to a prolonged soaking followed by a light brushing limited to the more robust wool-embroidered areas. This was indispensable for the removal of the greasy dirt and dust which had penetrated the wool-len fibres.

Once rinsed and dried, the textile appeared softer, and in many cases the wrinkles were less obvious. A great surprise was the extent to which the colours and fineness of detail in the embroidery were recovered: any loss of ink from the preparatory drawings was negligible.

##### 2. Support - Functional Problems

Once conservation of the panels had been completed they were to be remounted on the chairs. It was therefore necessary to be sure that the tension and stress of the work involved did not cause the weaker areas to be damaged further. Hence, it was decided to use a total support consisting of a plain-weave linen cloth whose weave was similar to that of the original canvas. The general rule that warp and weft of textile and support should correspond exactly was necessarily subjected to compromise due to the distortion of the embroidered panels (which could not be modified).

The textile was sewn to its support using stitches which passed over the crossing of a warp and weft thread of the canvas in those areas where this was left bare due to the loss of silk thread (the areas of sky in the landscape scenes and the lighter-coloured parts of the figures' clothes); where the embroidery was in good condition the stitch passed over either a warp or weft thread. By commencing stitching from the centre and proceeding towards the edges, it was possible to ensure that the support was adapted to the changes in relief of the reverse of the embroidery, particularly notable in those parts corresponding to the faces and other bare parts of the figures' bodies, due to the different embroidery technique used.

Sewing threads used for conservation were: 2-ply wool thread in the wool-worked areas and polyester thread (100/3) in the silk-worked areas. The latter was preferred to cotton thread due to its resistance to variations in Rh and temperature, particularly serious in Venice. The possibility of using the silk threads available was eliminated either because they were too glossy, too thick or insufficiently resistant to wear and tear.

##### 3. Support - Aesthetic Problems

The gaps and the tears in the canvas were rectified simply by repositioning the borders and fixing them to the support using the following method: the use of a support fabric dyed to a colour similar to that of the canvas was sufficient in these cases to recover the integrity of the ground to a satisfactory degree.

As for the areas subject to abrasion, a general rule was followed (although there were numerous exceptions to it). In the parts where large areas of silk had fallen away, the stitches did not cover the exposed canvas, although a coloured thread similar to the colour lost was used so as not to contribute further to the chromatic impoverishment of the object; a similar solution was employed for the smaller areas of wool lost due to the action of insects. Where, however, wear and tear had been such as to provoke considerable loss in the ground embroidered in black, a different procedure was used, due to the nature and the amount of the damage. If the damage was limited and the outlines of the decorative motifs certain (fig. 3), the embroidery was partially re-worked (in petit-point stitch rather than cross-stitch, using a fine black wool thread), following the indications provided by the fragmentary elements left by the original stitches (fig. 4); this procedure rendered the light-toned patches of colour

(due to the exposure of the canvas) less noticeable and imparted a greater vibrancy of tone to the surface itself. Where the damage was more extensive, the outline incomplete or the canvas also worn away (fig. 5), the stitching was limited to couching around the motif with fine black wool thread: this renewed structure of the decoration and also partly reconstructed the difference in relief between motif and background (fig. 6).

The tapestry strips were substituted by other strips of plain-weave wool dyed a suitable shade of black. This fabric was used double so as to make up for the difference in level between the canvas and the embroidered surface. It was whip-stitched into place with stitches worked closely together.

#### 4. Re-Assembly

Following a series of photographs of the finished pieces, the panels were reattached to the chairs (which in the meantime had themselves been the object of conservation). New, suitably-dyed linings and braids were used.

Since it was not possible to situate these objects behind glass (Ca' Rezzonico retains its character of a historic home) it was necessary to devise some other form of protection: a detachable polythene cover with cotton fabric borders (apart from conferring a greater strength to the covers, the visual impression conveyed became less obviously that of a plastic bag) was affixed to the chairs with tapes.

Braids, trimmings, linings and tacks from the previous work were retained as documentation; examples were also included with the conservation report.

#### Notes

1. Patron and author of the chairs are identified by an inscription carved on console: "Petri Venerii Iussu Andreas Brustolon fecit."  
For information relating to the Brustolon chairs, see Clelia Alberici, Il mobile veneziano, Milano, 1980; G. Mariacher, Ca' Rezzonico. Guida illustrata, Venice, 1969 (2nd ed.).
2. The only date known for certain is that carved on the base of one of the life-size warriors: "1706 AND<sup>S</sup> BRUSTOLO<sup>S</sup> BELL<sup>L</sup>. IS. F."; but it is probable that the entire group took more than 10 years to complete.
3. The pattern is close to that of some embroidered panels (late 17th - early 18th centuries) mounted on a group of chairs in the Musei Civici d'Arte Antica, Turin (see L. Malle, Mobili e arredi lignei. Arazzi e bozzetti per arazzi, Turin, 1972, pls. 187, 193 and 194. See also V. Viale, Mostra del Barocco piemontese, exhibition catalogue (Turin, 1963), Vol. III, Turin, 1963). One panel of a completely different decorative theme also exists: birds fly across a background of stylized vegetable motifs. The pattern resembles that of another group of chairs in the Turin Museum (see L. Malle, op. cit., pls. 188, 197-201).



## SUMMARY

The following paper contains an introduction to the final year projects of six third year students who will complete the post-graduate diploma course in textile conservation in July 1987. The students work on their projects between October and May, including basic historic research, scientific analysis and full conservation treatment. A written report is submitted at the end and stored in the Centre's Library. The objects conserved belong to museums and private clients and part of the project is to liaise with them and balance the conservation needs of the object with the client request.

A wide range of objects is being conserved this year; they are:

1. An Egyptian Grave Shroud  
Carla Petchek
2. A Tapestry Fragment  
Sarah Gates
3. A Raised Work Box  
Mary Jose
4. A Raised Beadwork Picture  
Caroline Muir
5. Two American Revolutionary Banners
6. A Military Flag or Guidon  
Irene Kirkwood

## SIX CASE STUDIES FROM A POST-GRADUATE TEXTILE TRAINING PROGRAMME

Margaret Roberts  
Textile Conservation Centre  
Apartment 22, Hampton Court Palace  
East Molesey  
Surrey. KT8 9AU

1. Egyptian Shroud, Greco Roman Period

The grave shroud, made of linen with a painted decoration, was excavated at Hawara in Egypt by Flinders Petrie at the turn of the century and now belongs to the Petrie Museum in London. It is intended for display in the main hall of the museum where, due to lack of space, it will have to be shown vertically. The curator considers the most important aspect of the shroud to be its decorative painted surface. Strips of linen, which may be the body wrappings, still adhere to the reverse side by virtue of the resin with which they were impregnated. It is now in three pieces, probably the result of poor storage conditions. It is very brittle and creased, the creases having set hard and caused breaks in the fibres and paint surface. Of the three pieces, the two smaller ones had been stored together and show evidence of insect infestation; the larger piece, however, shows extensive mould growth. Displaced paint particles, resin and dirt rest on the surface of the shroud.

The main aims of conservation are to clean the painted surface and attempt to restore the shroud to its former shape. The shroud has 3-dimensional characteristics, notably the moulding of the fabric around the foot area, therefore, for the display it seems appropriate to think in terms of a moulded platform to support the shroud. This would be fairly straightforward if the shroud was to be shown laid horizontal but problematic in a vertical case.

2. Tapestry Fragment 2nd half 15thC.

This piece is approximately 1 metre square and probably woven in Tournai. It has wool warps and wool and silk wefts. It is probably from the centre of a larger tapestry depicting the 'Calydonian Boar Hunt' a complete example of which is in the Walker Art Gallery, Baltimore, U.S.A. The fragment had been on open display in a window recess for many decades and it is intended to re-display it after treatment.

This display in full sunlight for so long has rendered the fragment in an extremely brittle and degraded condition akin to that of many archaeological textiles. There are many areas of partial and total loss of both warps and wefts; much of the silk has broken away from the front and the dark brown wool has gone for the most part. The fading on the front is severe and there is particulate soiling overall. Many small fragments of fibre break off even with the absolute minimum of handling.

As this piece is in such a fragile condition questions arise as to whether traditional treatments for tapestry are appropriate, e.g. cleaning by vacuum suction, followed by wet cleaning, then support by couching on to linen so that the object may be hung vertically. It was felt by the student that a textile in this condition would at one time have been considered as a suitable candidate for lubrication. She decided to look into lubrication materials and techniques and drew up a questionnaire which was sent to 35 conservators in different countries about treatments past and present. Enquiries were also made of manufacturers and educational organisations to find out about lubricants in current use.

Providing a suitable support also presents problems - a method should be selected which would minimise the mechanical damage caused by stitching and yet perform the function of support on a long-term basis. The type of display is crucial to the type of treatment selected and it was decided to look into designs for an enclosed system of support and to discuss the benefits with the client.

3. Raised Work Box c.1665

This is a privately owned raised work box c1665. The box is made of wood covered on the outside with off-white, silk satin fabric embroidered with polychrome silk yarn in a variety of techniques. The interior of the box is lined with paper and the draw fronts decorated with wapped silk yarn. This kind of box is typical of its date, although it is not padded or 'raised' to a great degree.

The locks and hinges are made of copper alloys (brass) and silver

and the nails and wedges used to construct the box are iron. The owner intends to use the box.

The fabric on the box is very dirty, obviously weak and fragmented. The box had been discovered in an attic and is soiled with dirt and dust, watermarks and bird droppings. One of the panels, which had all been glued to the box, had been removed by the owner and washed prior to the present conservation; some improvement was evident but damage had been caused to the silk during its removal.

One of the first challenges was to devise a method of removing the panels without causing undue damage. After any cleaning there will be the problem of supporting the panels and re-applying them without adding any bulk. A traditional method used with Far Eastern textiles on wood, wheat starch and Japanese paper, was considered to be more appropriate than a textile support. The composition of the box will bring the student into contact with materials she has not encountered previously: the cleaning and repair of wood, cleaning of paper and the cleaning and stabilisation of metals. It is important, since the box may be used, even if only occasionally, that the functioning parts, like hinges, locks and handles, work satisfactorily.

#### 4. Raised Beadwork Picture 17thC.

A 17thC raised work picture executed mainly in polychrome glass beads on an off-white satin ground. It is privately owned and arrived at the Centre with a frame which is too small for the picture and as far as was known, was to be returned to a similar type of display in the owner's home. The motifs depicted in the picture are typical of the 17th c: a man and a woman in the centre surrounded by all kinds of animals, insects, fish, flowers and plants. The beads are worked into a mesh by a needle weaving technique constructed over wool padding. Other materials used in the construction are pearl and coral beads, wood as a padding for the faces and parchment used for the hands.

The picture is dirty and dusty; there are watermarks and other stains on the satin. The beads appear to be coated in a layer of grease to which dirt and dust have adhered. Although there are only a few breaks in the satin it is obvious that it is weak all over and that the weight of the beads and padding have caused stress and damage. Repairs have been carried out previously using animal glue which has now discoloured. Poor framing has caused creases in the silk and there are sharp folds in some of the beaded area which were turned under to fit into the frame. The needlewoven mesh is for the most part intact but the silk thread is quite brittle and there are a few areas of insect damage where bead loss has occurred.

There is not much experience of working on beaded textiles at the Centre and in fact it is difficult to find any conservators who have worked on even one piece. The combination of materials and type of dirt presents problems in selecting an appropriate cleaning method. Many of the stains indicate the need for wet cleaning. However, parchment cannot be soaked and wetting the wood and wool may be problematic. The support of the textile will also need careful consideration as the ground stain is fine and structurally very weak yet has to support a comparatively immense weight. It was confirmed that the client wished the picture to be returned framed but had no particular attachment to the frame sent with it. Therefore, framing proposals are part of the student's brief.

#### 5. American Revolutionary Banners c.1779

Two from a set of four banners from the American Revolution, 1779, belonging to a private collection. Both of the banners are in excess of 1 metre square approximately and both had arrived folded in a glass front case measuring 1745 x 507 x 96mm. The first banner is yellow silk fabric with a central design of a beaver and a palmetto tree and thirteen silver-coloured stars in the blue inset canton; the second banner is blue silk fabric with the word 'Regiment' painted on it and a naturally frayed fringe at the fly edge. The banners are painted on both sides. It is intended that they should be returned to the same case for display.

Their cramped display conditions have rendered them very crumpled and crushed. They are dirty, dusty and stained but the owner had expressed an interest in the stains and did not want them removed lest they should be of historical importance, e.g. blood and powder burns. The yellow silk is in poor condition and approximately one quarter of this banner is missing. The paint is slightly powdery and cracked and the silk has fractured along the



splits in the paint. The blue silk is finer and in a more degraded condition, being generally weak with splits and holes. It appears to have deteriorated further in stained areas. Some holes seem to have burned edges. The painted areas have many splits and holes but the paint itself is in slightly better condition, being less powdery than on the yellow banner.

The cleaning of the banners presents interesting problems both because of compatibility of response of the silk and the paint, plus the proviso about the preservation of the stains. Relaxation of the silk and paint to attempt to flatten out the banners could be a long, slow process because of the severe folding and distortion, especially if wet cleaning is not a possibility.

The eventual display of the banners would have a strong influence on the treatment chosen and although the client had expressed a wish for them to be returned in their narrow box case, it was felt that excessive damage had been caused by this and that it was justifiable to draw up fresh proposals to display the banners flat and to proceed to discuss the merits of this with the client.

#### 6. Military Flag, early 19thC.

A small military flag called a guidon dating from the early 19th c. It is constructed of two layers of yellow silk fabric painted and gilded with similar military emblems on both sides and trimmed with a silver metal thread fringe. The owner has a sizeable collection of similar objects, some of which have been mounted, pressed between two sheets of glass.

The silk fabric of the guidon is degraded, both heavily soiled and fragile with many folds, splits and tears; this is probably a result of poor display and storage. Extensive repairs have been carried out, both patching and cobbling, which indicate that there are areas of original silk missing; this repair has also contributed to the distortion of the guidon. The paint is worn in places, e.g. on folds, but on the whole is adhering quite well to the silk. The fringe is extremely brittle with fragments breaking off very easily; some of the fringe is missing.

One of the main challenges is the problem posed by dealing with a double layered and double sided object. It makes any treatment far more technically complex. The heavy soiling indicates initially the desirability of a wet cleaning treatment, which would also aid the relaxing of the textile, but it will have to be established whether this would be compatible with the paint. Again, the eventual display will affect the choice of support. The client's choice of a pressured glass support will crush thicker areas like the fringe, yet leave the weakest areas, the silk, totally unsupported. It was decided that alternative methods of display should be proposed and discussed with the client.

With the development of facilities and the refinement of procedures over recent years, the Centre now offers a range of identification and analytical techniques. For more sophisticated tests the equipment or services of other institutions is often made available to us. Students and conservators alike are encouraged to see technical analysis as an additional tool which will help them make better informed decisions about treatment. Analysis is always undertaken with a view to its contribution towards greater knowledge of the object and appropriate treatment. In the more basic identification techniques, the results should support the conservators own judgments made during preliminary visual examination.

At the Centre the following tests and analyses can be carried out: fibre ID, yarn and weave analysis, dye analysis and thin layer chromatography (TLC), wet chemical metal ID, comparative pigment ID and paint cross sections, adhesive identification and leather identification.

The kind of analysis which can be arranged elsewhere includes X-ray fluorescence, infra-red spectrometry and X-ray diffraction; there is a continuing project on a variety of work with the scanning electron microscope. Extensive help has been forthcoming on fibre fracture through UMIST Fibre Science Department. A number of the projects this year are painted textiles (the Centre has worked on a large number of painted banners) and it is fortunate that our scientific tutor is a trained paintings conservator and that the Centre is a part of the Courtauld Institute and has the expertise of the staff and facilities of the paintings conservation department on hand.

The students on all these projects will carry out fibre identification and yarn and weave analysis where possible but from then on their paths will be dictated by the nature of the object and their ideas about treatment.

Conclusions: The paper shows the wide variety of materials worked on at the Centre and the six third year projects are a fairly representative sample of the problems which may be being worked on at any one time. Relating the analysis and identification techniques indicates the range of methods available to help conservators make informed decisions about treatment.

#### ACKNOWLEDGMENTS

I wish to thank the staff of the Textile Conservation Centre for their advice and the final year students as named in the text for their invaluable contributions to this paper.



## SUMMARY

Dyestuffs used in Hungarian folk textile dyeing may be divided into two major groups: first, vegetable, animal and synthetic dyes which were available commercially in the 18th, 19th and 20th century and second, dyeing plants which were indigenous where the textile was produced. Research aimed at the investigation of dyestuffs was extended to all the dyes listed in the contemporary dyeing recipes as well as subsequent ethnographical sources. Analysis by thin-layer chromatography, wet chemical tests, spectroscopic methods and X-ray diffraction was applied to all 122 reference dyes collected. Coloured yarns of two characteristic Hungarian folk textile groups were investigated by the same methods. Some of the results contradicted ethnographic studies on dyeing of yarns of Hungarian folk textiles. The evaluation of the results gave valuable information for ethnographers as well as for restorers.

## INVESTIGATION OF DYES ON HUNGARIAN FOLK TEXTILES

Ágnes Timár-Balázsy  
Conservation scientist  
National Centre of Museums  
Budapest 100, P.O.B. 54. 1476 Hungary

Introduction

Art historians and restorers permanently ask for the examination of the dyes found on museological textiles so that dating, the identification of forgeries and that of parts which belong together as well as an anticipation of the reactions of the dyes during cleaning and conservation can be carried out.

Since the majority of the textiles found in the Hungarian ethnographical collections date back to the 19th and 20th century and a lot of data may be gathered on the origins of the object during collection itself, it is only very rarely that the identification of dyes plays a part in dating. In order to find out what conclusions may be drawn from the results of the examination of dyes found on Hungarian folk textiles, research was aimed at the compilation and identification of dyeing agents applied in the colouring of Hungarian folk textiles. This was followed by the determination of dyes for two typically Hungarian object groups.

Dyes applied in the dyeing of Hungarian folk textiles

From the 18th century onwards the dyeing of folk textiles or that of threads decorating them took place in two ways which differed both in their state of development and the materials applied. In the manufactures or, later on, in the small workshops the dyeing of yarns and woven fabrics was carried out in accordance with precise recipes and the standard of the small-scale industry of the time [1]. On the other hand ethnographical studies describe how dyeing was carried out with vegetable dyes obtained from the plants around the house even at the beginning of this century [2,3]. There are data confirming that the influx of oriental dyes has started already during the Turkish rule [1536-1686] [4], and

- ▽ = sumac  
▼ = cristall tartarate  
⊙ = madder  
⊖ = sandel wood  
♀ = alum  
♀ = crem of tartar  
⊙ = cochineal  
⊙ = potassium carbonate  
⊙ = starch  
□ = fustic  
▣ = logwood  
○ = copper sulphate or ferrosulphate  
▽ = gall  
⊙ = sulphuric acid  
⊙ = copper sulphate  
▣ = young fustic  
A = aqua fortis  
▣ = red wood  
G.O. = darken by copper sulphate  
18s.l. = to boil for 1 hour  
etwas w.K. = some common salt

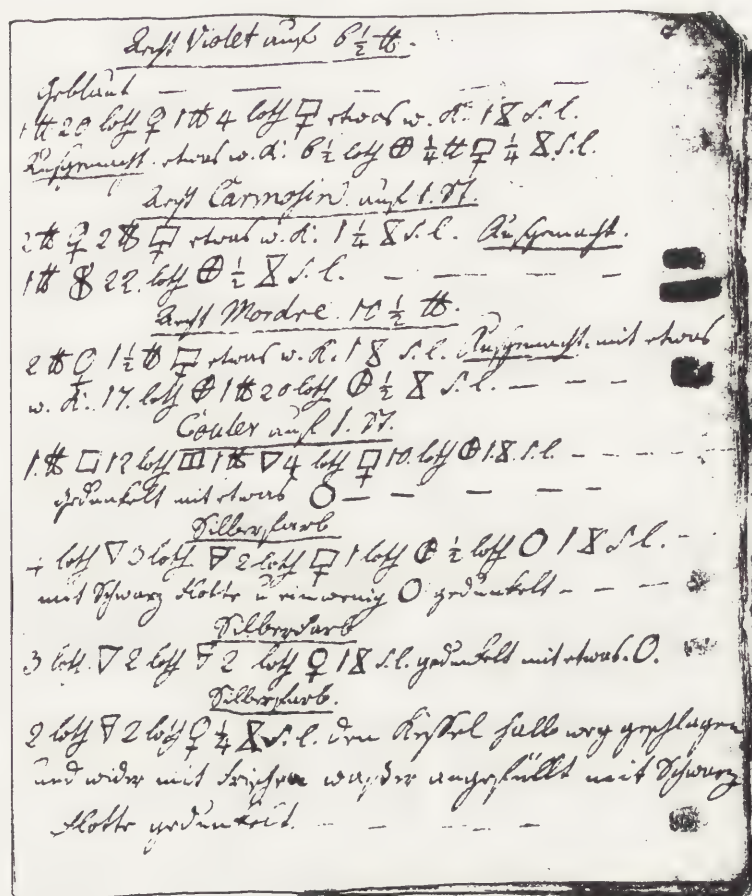


Fig.1: The clue of the ideography

Fig.2: A page of the Kluge manuscript /1809/ with the dyeing recipes written with ideography





Photo 1: cushion from the Great Plain



Photo 2: cushion from Orosháza



Photo 3: cushion from Ménes



Photo 4: cushion from the Great Plain

that there were ample opportunities to buy a great many imported dyes in the shops later on /5/.

The most valuable textile dyeing recipe collections of Hungarian origin have been passed on us from the turn of the 18th-19th century. In the Pápa workshop textile dyeing was based on the manuscript prepared by Károly Kluge in Sorau, Saxony /1782/ and Károly Kluge jr. in Lindau /1809/. Apart from the recipes /Figure 2/ a valuable source to be found in the second manuscript is the table containing the keys to the symbols and substances used /Figure 1/.

Therefore, for example, the resolution of the recipe "Rohfarb" is as follows:

8 loth □ 14 loth ▯ 8 loth ⊕ 2 lt ∇ 1 ⚡ s.l.G.O.

8 loth fustic, 14 loth logwood, 8 loth madder, 2 pounds of sumac to be allowed to boil for one hour. Darkening with copper sulphate solution /6/. /1 loth = half an ounce/

A collection of dyeing recipes from the beginning of the 19th century probably originated from Transylvania refers to vegetable dyes like wild marjoram, the leaves of crab-apple tree, elderberry, dyer's saw-wort, young fustic, oak apples and alder tree bark. Furthermore, it contains formulas for the production of Prussian blue on textile as well as for dyeing by indigo, Brazil wood, logwood and annato /7/.

Books from the same period - namely 1809 - containing the description of various techniques enumerate the following dyes used in Hungary: cochineal, madder, alkanet root, safflower, Brazil-wood, dyer's saw-wort, weld, dyer's greenweed, mulberry, yellow ginger, rhubarb, annato, indigo, woad, logwood, oak apples, alder tree bark, shell of walnut /8/.

Györfy wrote a comprehensive series of articles in the 1921 issues of HERBA on folk textile dyeing with domestic plants /9/ Besides enumerating all the important indigenous dyeing plants, he refers to recipes noted down as used in practice. The majority of the recipes originated in Transylvania, a region where the isolated Hungarian communities had retained the folk traditions most intact.

To obtain black and brown alder tree, walnut tree, wild marjoram, common maple, elderberry, oak, common ash, plum-tree, apple tree, nightshade, lady's thumb, bean, logwood, young fustic, privet and pulmonia were used on iron or iron and alum mordant.

Yellow was obtained from dyer's green-weed, dyer's anthemis, safflower, weld, yellow cudweed, wild marjoram, cypress-spurge, nettle, lion's tooth, common mustard, saffron, onion, tobacco, oat, buckthorn, young fustic, mulberry tree, apple tree, pear tree, willow wood, common white birch, privet, wild orange, garden sorrel, spindle berry, cyttisus, elder tree, alder tree and grape, mostly on alum and tartaric mordant.

Blue was produced from woad, violet, Spanish garlic and wild saffron. Red was obtained from madder, alkanet root, apple tree, plum tree, alder tree, safflower, perforated hypericon, pigeon berry, common maple and Polish cochineal.

Vámszer reported in a 1921 issue of HERBA that for the dyeing of threads employed to produce the "Csik" caprets commercial /aniline or coal-tar/ dyes had been used for the previous 20-30 years instead of vegetable dyes, since they were relatively cheap and there was no need to take the trouble of picking the scattered plants and boiling them /10/.

#### Collection of reference dyes

With the help of the Herbaria Medicinal Plant Company and the University of Horticulture it was possible to gather the bulk of the dyeing plants listed and described in the above mentioned literary sources. Textile dyes which were widely used in Europe in the 18th-19th century were received from the Central Research Laboratory in Amsterdam.

#### Dyeing with the collected dyes

Before starting on the chemical investigations it was deemed necessary to reproduce the recipes given in the technical literature. Our aim was not solely to obtain the given hue, but to obtain the dye on the reference sample just as it is on the unknown one, namely after dyeing. Not all dyeing components to be found in the dyeing plants or the brew of their dried drug or





Photo 5: cushion from Karcag



Photo 6: cushion from Orosháza

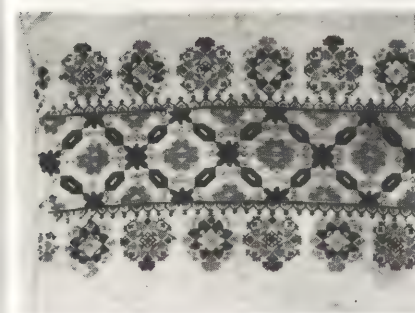


Photo 7: cushion from the Great Plain

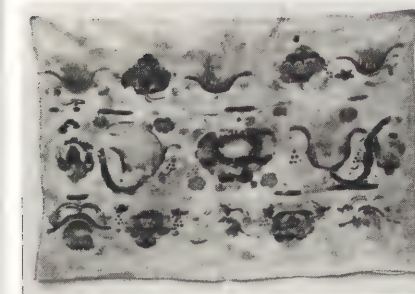


Photo 8: cushion from the Great Plain

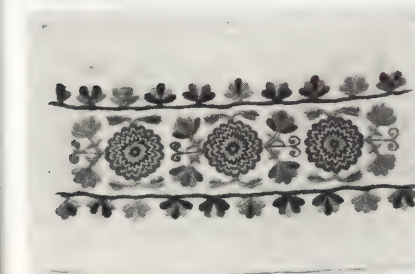


Photo 9: cushion from Kunmadaras

fermented liquid will get fixed on the textile or thread to be dyed. It would be misleading therefore, if in the course of comparison we were to look for components which are rightfully missing - as a result of the dyeing conditions.

Dyeing took place following the recipes from the end of the last century, collected by Györfy /9/ and the modern recipes published in recent decades reviving the traditions of dyeing by natural dyes /11, 12, 13, 14/.

#### Identification of vegetable and animal dyes

#### Investigation by thin-layer chromatography

Dyed samples with alizarin, purpurin, madder, cochineal, kermes, Polish cochineal, lack-dye, alkanet root, archil, gudbear, Brazil-wood, sandel wood, dragon's blood, oak, oak apple, henna, tannic, logwood, carthamin, safflower, elderberry, walnut, chamomile, mallow, red poppy gave an appreciable chromatogram in the same chromatographic conditions. Cellulose-acetate 300 Ac-10 /Macherey-Nagel/ layer, ethyl acetate: tetrahydrofuran: water = 6:35:45 eluent system /15/ was found to work best with a slight alteration, namely ethyl acetate was replaced by methylformiate in the same proportion. In this manner I was able to avoid the difficulties in mixing while preparing the solution but the same good separation was obtained. For detecting 0.5 M alcoholic KOH and illumination by UV/350 was used.

Without aiming at the determination of their chemical structure the system suited for the investigation of flavonoids proved to be appropriate for the identification a number of other native dyestuffs: Kieselgel 60 DC-Alufolien /Merck/ layer, chloroform: ethyl acetate: methyl ethyl ketone: formic acid = 15:5:3:1 eluent, 1% Naturstoffreagens /2-amino-diphenil borate/ + UV/350 detection /16/.

Samples dyed with apigenin, luteolin, weld, dyer's sawwort, dyer's greenweed, Persian berries, rhamnetin, dyer's buckthorn, kaempferol, kaempferid, emodin, aloe, alder tree, garden sorrel, persicaria, maclurin, morin, fustic, soranji, fizetin, young fustic, quercetin, onion, quercitrin, quercitron, rutin, acacia, Japanese sophora, pigeonberry, nettle, common cytiscus, agrimony, common juniper, cornflower, chrisin, bilberry, willow wood, haw, chestnut, pomegranate, oak apple, lion's tooth, cudweed, Indian yellow, Island lichen, common ash, common marigold, cypress-spurge medic, perforated hypericon, horseshoe, common white birch, elecampane, red poppy, goose-grass, quebracho, safflower, dogwood, ulmus, leaf of grape, wild marjoram, sumac, tee, large chevril, pulmonaria, tansy gave a characteristic chromatogram in that chromatographic condition.

For samples dyed with crocetin, saffron, bixin, annato, carrot and common marigold which belong to or have a related structure to the group of carotinoids the following system was found to work well: Kieselgel 60 F<sub>254</sub> /Merck/, eluent: benzol-methanol-ether = 85:5:10, detection: I. spraying by 5% Rhodanin in ethanol; II. spraying by 25% ammonia, observation in UV/254 nm light /17/.

Preparation of both the known and the unknown samples consisted of boiling a fibre samples about 1 mm in length with a drop of 10% hydrochloric acid, dissolving the dye in methylated spirit and applied onto the layer by capillary action.

#### Investigation by wet analysis

The detection of indigo was carried out by wet analytical test tube reactions in the course of which the sample was treated by hot, alkaline sodium-dithionite after cooling a drop of ethyl acetate added to it. If the upper ethyl acetate layer turned blue, the presence of indigo was confirmed /18/.

#### Investigation by spectroscopic method

For the tracing of indigo carmine /indigo-disulfonic-acid/ the UV/visible light spectroscopic method was chosen /19/. The about 1 mm sample dyed with indigo carmine was boiled with acidified methanol for 20 minutes. On the UV/visible spectrum it gave a peak at 609 nm.

#### Investigation by X-ray diffraction

For the experiments aimed at tracing Prussian blue reference material of my own making was applied: the textile was first





Photo 10: cushion from the Great Plain



Photo 11: cushion from Hódmezővásárhely



Photo 12: cushion edge from the Great Plain



Photo 13: carpet from Transylvania

impregnated by potassium ferrocyanide, then immersed in ferrous sulphate and subsequently the coloured fibre sample was examined by X-ray diffraction. Agfa D7 film was used for the photos taken in a 114.6 Debye-Sherrer chamber with an exposure time of 3 hours. Induction was brought about by a copper anode X-ray tube fitted with nickel filter at 40 kV voltage and 60 mA amperage. A 2 mm long fibre was drawn into the small glass tube. The same procedure was applied on the unknown samples where during wet analysis the probability of the presence of Prussian blue emerged.

#### Identification of synthetic dyes

When investigating synthetic dyes we did not aim at determining each individual dye; instead, groups of direct, basic, acidic and mordant dyes were distinguished after treating them with the reagent series /distilled water, ethanol, ammonia and glacial acetic acid/ as well as based on the results of dyeing tests suggested by Schweppe /20/.

#### Results of dye analysis on embroideries from the southern part of the Great Hungarian Plain

Pieces of woollen needlework belong to the oldest peasant embroideries that have survived in Hungary. Plain black and coloured embroideries were used in the southern part of Transdanubia and the Highlands to decorate hemlines of sheets and the edges of cushions in the Great Hungarian Plain. Cumanian embroideries are characterized by a rich variety of hues rust-red to pink, beige to brown and light-green to dark-green; relatively little black is used. As for the embroideries from Hódmezővásárhely, predominantly beige, pink and blue hues were used with golden brown, a kind of colder brown, rose red and 5-6 shades of corn-flower blue. Plain cushion selvages embroidered by black woollen yarn faded to brown by now have also remained. /21/

Fourtynine samples taken from 20 cushions from the collection of the Ethnographical Museum were investigated by the above reported methods.

On the yellow yarns weld, persicaria, safflower, chamomile, on the red ones cochineal or madder were identified. The brown coloured yarns were dyed with persicaria, black with eldertree root, logwood or tannic, blue with indigo or logwood, green with weld and indigo.

Since madder is not indigenous in the Great Hungarian Plain both the madder and the cochineal could have been bought in the shops or from tradesmen. When tracing red dyes, it was observed that in particular regions the same dye was traded, or women seem to have been able to handle one particular sort better. On the red yarns of the cushions from Karcag only cochineal was found while on those from Orosháza only red yarns dyed with madder were identified.

In each region a great variety of plants might have been used to obtain yellow, brown and black colours. This may have been the reason for the failure to identify some of this dyes, since among our reference materials only plants occurring in the recipes were found.

#### Results of dye analysis on carpets from Transylvania

In the homes of Hungarians in Eastern Transylvania and Moldavia one often comes across a kind of wollen blanket resembling a small sized oriental carpet which was called "coloured" in order to distinguish it from all the ordinary blankets decorated only by a couple of coloured stripes at the most. This blankets are characterized by the usage of greenish ochre, dark blue colours, and natural white pattern are found on a rusty-brown or onion brown base /22/.

Thirty-four samples were taken from 8 19th-century "coloured" blankets in the collection of the Ethnographical Museum and investigated by the above reported methods.

Although madder grow abundantly in Transylvania, its presence was not detected on any of the investigated objects. As red dyes cochineal and henna were identified. On the yellow yarns weld, on the green ones fustic with indigo was found. Brown was achieved by dyeing with henna or tannic. Among the blue yarns which were dyed with indigo mainly, two was found to have been dyed with Prussian blue; this latter would have been difficult to produce domestically. There were some blankets where synthetic basic and acid dyes were found together with yarns dyed with natural dyes.





Photo 14: carpet from Transylvania

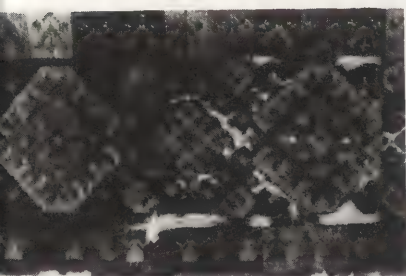


Photo 15: detail of a carpet from Transylvania, yarns dyed with synthetic dyes



Photo 16: carpet from Transylvania

This facts seems to contradict written sources which claim that the yarns of the "coloured" blankets were always dyed domestically with plants around the homes.

Only synthetic dyes were found on the yellow, orange, violet, claret, red, dark violet, violet-blue, light and dark green yarns of one blanket. The blue yarns were dyed with indigo. According to the results of dyeing tests, the phosphorescent violet dye belonged to the "direct", the yellow, orange, red and claret dyes to the "acid" and the green and dark violet dyes to the "basic" group of dyes. Basic and acid dyes were among the early synthetic dyes. But the first "direct" synthetic dye, the Congo Red /Direct Red 28, 22120 C.O./ was discovered in 1884, it may be supposed that the blanket could not have been made earlier.

As all the dyes of this latter blanket were dissolved both in distilled water and in organic solvents the restorer gave up cleaning the object.

#### Summary of the results

Investigation of dyes on folk textiles brought unexpected results wich partly contradict ethnographic studies claming that the yarns of ethnographic textile were always dyed with plants indigenous on the field the object was made. The results have proved that the bulk of the dyestuffs used in the dyeing of the investigated textiles was made up of dyes obtained commercially, even if there were dyeing plants providing a similar hue in the region.

On objects produced in the same region similar dyes were identified consistently.

Suprisingly, during the analyses we have not come across fibre samples containing several dyes /except green/, although very often the application of several natural dyes in the same dye bath is mentioned in the recipes.

Based on the identification of natural dyes whose chemical structure is known as well as the grouping of synthetic dyes, the restorer was provided with important information on the possibilities of bleeding or change in colour.

Results arrived at by research on the reference materials can serve as a convenient starting point for the investigation of further Hungarian ethnographical textiles.

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#### References

1. Domonkos O.: A magyarországi kékfestés, /Blue dyeing in Hungary/, Corvina, 1981. 174.
2. Miklóssy V.: "Festőnövények a csiki háziiparban", /Dyeing plants in the domestic industry in Csik/, Népismereti dolgozatok, Kriterion, 1978, 91-93.
3. Boros Á., Szabó L.: "Hazai festőnövényeink", Indigenous dyeing plants in Hungary/, Buvár 3, 1973, 142-147.
4. Györfly I.: "A hazai festőnövények és a velük való népi festési módok", /Indigenous dyeing plants in Hungary and folk dyeing methods/, Herba I, 1921, 9-10.
5. Frecskay J.: Ismeretek a kézmű és műipar mezejéről, /Knowledge from the field of craft and industry/, 1879, 98-116.

6. Kluge K.: Manuscript of dyeing recipes, Lindau, 1809, 78.
7. Ráduly E.: "Egy XIX. század eleji festék-recept gyűjtemény" /A collection of dyeing recipes from the beginning of the 19th century/, A Debreceni Déri Múzeum Évkönyve, 1977, 335-345.
8. Gergelyffy A.: Technológia, vagyis a mesterségek és némely alkotmányok rövid leírása, /Technology, namely short description of crafts and some constructions/, Pozsony, 1809, 36-44.
9. Győrffy I.: "A hazai festőnövények és a velük való népi festési módok", /Indigenous dyeing plants in Hungary and folk dyeing methods/, Herba I-II 1921, 11-94.
10. Vámszer G.: "A csiki szőnyegek festőanyaga", /Dyeing materials of the Csik carpets/, Herba IV 1922, 25-26.
11. Robertson, S.: Dyes from Plants, Van Nostrand Reinhold Comp. 1973, 144.
12. Spranger, E.: Färbbuch. Grundlagen der Pflanzenfärberei auf Wolle, Eugen Rentsch Verlag, 1975 157.
13. Fieler, G.: Farben aus der Natur, M. H. Schaper, 1978, 168.
14. Smeets, F.: Wol en Plantaardig Verven, Cantecleer bv, de bilt 1975, 70.
15. Hofenk de Graaff, J.H.: "On the Occurrence of Red Dyestuff in Textile Materials from the Period 1450-1600", ICOM Committee for Conservation, Plenary Meeting, October 2-5, Madrid 1972, 35.
16. Hofenk de Graaff, J.H., Roelofs, W.: "The Analysis of Flavonoids in Natural Yellow Dyestuffs occurring in Ancient Textiles", ICOM Committee for Conservation 5th Triennial Meeting, Zagreb 1978/9/4 15.
17. Stahl, E.: Dünnschichtchromatographie, Springer Verlag, 1967, 979.
18. Hofenk de Graaff, J.H.: "A simple method for the Identification of Indigo", Studies in Conservation 19, 1974, 54-55.
19. Dalrymple, H.E.: "A Seventeenth Century Dance Costume: Results of Analysis", The Laboratories of the National Museum of Antiquities of Scotland Volume 2 1984, 111-117.
20. Schweppe, H.: "Identification of dyes on Old Textiles", Journal of the American Institute for Conservation 19 1980, 14-23.
21. Knotik M.: "Szabadrajzu szőrös párnavégek a Dél-Alföldön", /Free drawn embroidered cushions from the southern part of the Great Hungarian Plain/, A Móra Ferenc Múzeum Évkönyve, Szeged, 1970, 119-155.
22. Szentimrei, J.: "Székely festékesek", /Coloured blankets from Transylvania/, Népművészeti füzetek, Állami Irodalmi és Művészeti Kiadó, 1957, 47.



## SUMMARY

A questionnaire on the treatment of painted flags and banners was sent to a total of 81 conservators in the UK and overseas, to assess past and present conservation techniques used to treat these objects. Questions on cleaning, consolidation, relaxation, conservation methods (ie. stitching versus sticking), storage and display techniques were included. The paper summarises the results from the thirty completed questionnaires that were returned and brings together points for further discussion and research.

## RESULTS FROM A QUESTIONNAIRE ON THE CONSERVATION TREATMENT OF PAINTED FLAGS AND BANNERS

N.S. Yates  
Textile Conservator  
National Maritime Museum,  
Greenwich,  
London SE10 9NF, England.

Introduction

The purpose of this survey was to discover the past and present conservation techniques used to treat painted flags and banners. These items cause conservators many problems because of the diversity of materials used in flag making, and the difficulties of handling what are often very large, fragile objects. We felt that a questionnaire of this kind would act as a good starting point on which to base research into this area, and the questions and results might be of interest to other conservators who have to deal with them.

After initial contact, a total of sixteen questionnaires were sent to practising textile conservators in Britain and a further sixty-five were sent to twenty countries abroad. We received nine completed questionnaires from Britain and twenty-one from abroad and these form the basis of the results.

The results have been compiled entirely from the answers received from participating conservators and it should be noted that names of products, and/or equipment are those specified by the conservators. They may, therefore, be different commercial names for the same product.

Results1. DO YOU GENERALLY WASH YOUR PAINTED TEXTILES?

We asked this question because the washing procedure is frequently carried out almost as a matter of course to unpainted textiles (after testing dyes etc.) without harm, but it is a potentially hazardous operation when applied to paint, and as such we were interested to see how many conservators consider this treatment. The majority (20 out of 27) preferred to wash their flags whenever possible, but this was generally dependent on the results from careful testing and examination of the paint and fabric, and the application of any necessary pre-treatments (such as consolidation) of painted areas.

2. DO YOU TEST THE PAINT BEFORE WASHING? IF YES, WHAT METHODS DO YOU USE?

All those that considered washing their textiles reported that they carry out some form of testing beforehand. The majority carried out tests on both paint and textile although one conservator reported testing the fabric only but consolidated some painted areas prior to washing. The following methods of examination were mentioned.

- a) Visual and microscopic examination to establish the nature of the medium in which the paint is applied and the condition of the paint layers and textile. Cross-sections through paint layers were also mentioned.
- b) One conservator mentioned the use of more sophisticated analytical techniques including, chemical analysis, spectrographic analysis, thin layer chromatography (TLC), as a means of determining media type and dyes.
- c) The solubility of paint layers was generally determined by the application of swabs, pellets of cotton wool or blotting paper dampened with water and/or the proposed washing solution which were then either left in position or gently rolled on the surface. Other solvents used for testing included white spirit and organic solvents in general. Ninhydrin was mentioned as a means of testing the layers of paint for the presence of protein, and therefore indicating its solubility in water. Close visual and microscopic examinations were used to determine the results of these tests.
- d) The adherence of the paint layers was generally determined by rolling a swab of cotton-wool dampened with water or water and washing solution over the surface of the paint. Gently rubbing with a soft brush wetted with washing solution on the most fragile areas, was also mentioned.

- e) The strength and acidity of the unpainted areas was occasionally assessed.

3. HAVE YOU NOTICED ANY PAINT LOSS DURING WASHING?

Of the 20 conservators that considered washing flags, 14 had noticed some slight paint loss during the washing process. It was found to occur more frequently when the washing process was prolonged. In one case the painted fabric was found to crack and chip off completely. Most conservators believed that, provided a pre-treatment (such as consolidation) was carried out, there would not be any paint loss. Finest 'Bondina' was mentioned as giving more protection against rubbing than nylon net during washing.

4. IF THE FLAG IS NOT WASHED DO YOU USE OTHER METHODS FOR CLEANING THE TEXTILE AND/OR PAINT? IF YES, WHICH METHODS?

Six conservators said that as yet this had not arisen or that they do not use other methods for cleaning the textile and/or paint. The remaining 24 conservators used a variety of methods; several mentioned the separate cleaning of painted areas, which sometimes included varnish removal. Enzymes, water, detergent solutions, a variety of solvents and saliva were all mentioned for specific use on paint. Other general non-aqueous cleaning methods included; - Vacuuming, aspirating, opaline pads, brushing, tamping with a dry sponge, spot cleaning on cold table, local treatment with detergent solutions, barely moist cotton, mechanical methods over barely absolved cotton, use of a 'groom-stik', (a molecular trap), damp blotters and towels to remove loose dirt. Dry cleaning with solvents was also mentioned in a few cases.

5. DO YOU EVER USE CONSOLIDATION TECHNIQUES ON THE PAINTED AREAS?

20 conservators have used or would consider using consolidants provided they were necessary. One conservator mentioned the importance of maintaining the drape of a banner when considering consolidation. Another also mentioned that they would only consolidate a banner on the condition that it will never be bent or distorted in the future and that it should then be encased in a 'trap' or box permanently. One observed that sandwiching between two fabrics appeared to be more useful, while another conservator said she had used a consolidant once, but never would again; (reasons not given).

IF YES, ARE THEY APPLIED BEFORE OR AFTER WASHING?

12 out of 20 conservators applied consolidants before washing, a further 2 considered applying before and after, depending on the particular object and adhesive, while a further 4 said that they generally apply them after washing. Another conservator had previously consolidated paint after washing but would like to try applying it before. The remainder either never apply consolidants or did not reply to this section.

WHAT CONSOLIDANTS HAVE YOU USED AND IN WHAT CONCENTRATIONS?

The following have been used;-

- |   |   |
|---|---|
| a) Paraloid B72<br>(acrylic polymer)    | 5% in toluene<br>5% in unspecified solvent<br>(applied as a spray)<br>5% " " "<br>2%, 5% and 10% in xylene<br>2% in ethyl alcohol (IMS) -<br>applied by brush by 2 people<br>4% in ethyl alcohol (IMS) -<br>applied as a spray<br>3% - 5% in acetone (used by 2<br>people)<br>Less than 5% in ethanol<br>2% in petroleum spirit<br>5% in petroleum spirit<br>15% - 20% (used by two people) |
| b) Paraloid B67<br>(acrylic polymer)    | Unspecified concentration   |
| c) Primal A235<br>(acrylic polymer)     | Medium matt no.2 in water 1:1   |
| d) Plexisol<br>(acrylic polymer)        | Unspecified concentrations in<br>ethyl alcohol  |
| e) Rowney Cryla<br>(acrylic polymer)    | Different concentrations, diluted<br>with water (applied by brush and<br>spray - used by 2 people.  |
| f) Mowital B60HH<br>(polyvinyl butyral) |   |
| g) Polyvinyl acetate<br>emulsion        |   |



- h) Beva 371 (ethylene vinyl acetate co-polymer) - Unspecified concentrations (used by four people)
- i) Klucel (hydroxypropyl cellulose) - 10% in unspecified diluent
- j) Cellulose based consolidants such as carboxymethyl cellulose - unknown concentration (used by two people).
- k) Soluble nylon - Unspecified concentration  
2% in ethyl alcohol (IMS)
- l) Beeswax in toluene - Unspecified concentration
- m) 'Zapone' (Danish) - Unspecified lacquer in 20% solution with acetone (now advised not to use by paintings conservators because of yellowing)

WERE YOU SATISFIED WITH THE RESULTS? IF NOT WHY NOT?

Sources held varying opinions about the success of the consolidants, although most were generally satisfied with results. Soluble nylon was found to be satisfactory by one conservator while another felt that it had hardened the surface and changed the character of the fabric. Paraloid B72 and Polyvinyl Butyral also caused differences in opinion. Beva 371 had been found successful in holding flaking paint, but was not ideal in other unspecified respects. The results from beeswax in toluene, polyvinyl alcohol and Klucel were found to be unsatisfactory, although no one specified why.

6. DO YOU EVER USE ANY RELAXATION TECHNIQUES TO FLATTEN DISTORTED PAINT?

12 conservators stated that they either do not use any form of relaxation techniques to flatten distorted paint or that they have never needed to up to now. The remaining numbers use relaxation techniques, or rely on washing to provide the required humidity.

IF YES, WHAT METHODS DO YOU USE AND ARE THESE APPLIED BEFORE OR AFTER WASHING?

The most frequently used method utilised the aqueous cleaning process itself as a means of relaxing the distorted paint by smoothing and aligning areas while the paint and fabric were still damp. This may involve the use of pins, polythene straps and glass plates etc. to hold the aligned fabric in position, provided the fabric was strong enough. Several conservators mentioned using relaxation techniques prior to washing, these included pre-humidification in an R.H. chamber and the application of lauryl alcohol/dodecanol which is applied by brushing over the surface and then heated to 100° - 120°C (1) (Authors' note: this procedure may be hazardous to the paint and to the conservator).

The other methods were applied after cleaning and included combinations of pressure, heat and/or moisture, local humidification (if only small areas were painted), and general raised humidity within some form of constructed chamber. Two conservators have also used beeswax in toluene. This was applied warm to the painted surface and after covering with Melinex (polyester film) it would be weighted with glass plates and left overnight.

Mention was also made of the desirability of a cold air flow table. The following comments were made concerning the use of raised humidity: "If a flag is mainly painted, showing very little textile. Relaxing in a tent (with raised humidity) may provoke fungus growth if not watched, the surface needs to be cleaned before humidification. Often the top layer of paint is not sensitive to moisture but the bottom layer often is, this allows the textile to relax but, the amount of moisture has to be well evaluated so as not to cause disturbance to the painted top layer. At this stage, handling has to be done carefully and progressively."

7a) WHAT TYPE OF SUPPORT FABRICS HAVE YOU USED IN ORDER OF PREFERENCE AND HAS THE CHOICE BEEN AFFECTED BY THE TYPE OF TEXTILE FIBRE INVOLVED?

The following have been used as support fabrics (in order of preference):  
Silk Crepeline  
Polyester Stabiltex in a variety of weights  
Nylon net  
Cotton fabrics in various weights  
Polyester fabrics (including polyester batting beneath the textile)

Wool  
Linen  
Japanese paper

The choice of fabric was determined by:

- The type of textile fibre involved. People often mentioned preferring to use like with like fabrics ie. similar fabric type to the original object.
- The environmental conditions in which the textile would be stored and displayed; this was a particularly important consideration in some countries with very variable RH levels and would often lead to the use of synthetic support fabrics.
- Polyester Stabiltex and silk Crepeline were mentioned as being particularly useful in conjunction with adhesive lining techniques.
- The final mounting technique and method of display also played an important role in the choice of support fabric.
- The weight and drape of the original object was an important consideration.
- The type of decoration on the object eg. painted or embroidered etc.
- Visual and tactile considerations.
- The strength required of the support fabric - depending on weight and condition of object.

7b) DO DOUBLE SIDED PAINTED TEXTILES AFFECT THIS CHOICE, AND HOW?

The majority of conservators (24 out of 30) felt their choice of support fabrics would probably be affected by the double-sided nature of some painted textiles. It was felt that, where possible, semi-transparent fabrics such as silk Crepeline and polyester Stabiltex should be used so that both sides remain visible. Depending on the condition of the object, and storage or display requirements, one side may be obscured by the addition of a reconstruction, lining or padded display board. However, these could be easily removed at anytime to reveal the covered side. Two conservators also mentioned the importance of localised treatments where possible, instead of a complete backing fabric.

8. DO YOU USE STICKING METHODS, STITCHING METHODS OR A COMBINATION OF BOTH?

The majority of conservators used a combination of methods but tended to prefer stitching if the condition of the object allowed. Several conservators mentioned that their use of adhesives was mainly in conjunction with the painted textiles. Two conservators preferred to use pressure techniques where possible (ie. sandwiching between glass and backboard to obviate the need of stitching or sticking, although care must be taken when this is used in conjunction with painted textiles because the paint can stick to the glass).

One person mentioned that she used to use sticking methods 8 - 10 years ago, but rarely does now, (no reasons given).

9. STICKING METHODS

WHAT ADHESIVES HAVE YOU USED AND IN WHAT RATIO TO SOLVENT?

The following adhesives have been used:-

- |    |  |  |
|----|--|--|
| a) | Mowilith DMV1 and DM5 (1969-1975)  | - 1DMV1 : 1DM5 : 2 water (polyvinyl acetate)   |
| b) | Mowilith DMC2 (from 1976)  | - used in varying proportions with de-ionised water, from 10% - 40% depending on the required use. |
|    | Mowilith DMC2 has also been mixed in equal parts with Mowilith DM5, and in the same proportions with Vinnapas EP1. |  |
| c) | Vinnapas EP1 (polyvinyl acetate)   | - is used in varying proportions, 2%-40%, depending on required use.                               |
| d) | Vinamul 6525 (polyvinyl acetate)   | - diluted with de-ionised water in different ratios.   |
| e) | Vinamul 6815 (polyvinyl acetate)   | - " " "  |
| f) | AYAA and AYAC (polyvinyl acetates)   | - equal proportions of AYAA and AYAC in 2% soln.   |
| g) | Paraloid F16 (acrylic polymer)   | - 1 paraloid : 7/8 toluene   |
| h) | Paraloid F10 (acrylic polymer)   | - 1 paraloid : 7 solvent unspecified<br>1 paraloid : 8 toluene                                     |



- |    |   |   |   |
|----|---|---|---|
| i) | Carboxymethyl cellulose                         | - | ratios vary                                       |
| j) | Methylhydroxy ethylcellulose                    | - | ratios vary                                       |
| k) | Starch and modified starch pastes               | - | unspecified concentrations                        |
| l) | Mowital B60H<br>(polyvinyl butyral)             | - | 0.5% - 1.5% in ethyl alcohol                      |
| m) | Calaton CB<br>(soluble nylon)                   | - | 2% solution in alcohol or solvent                 |
| n) | Beva 371<br>(ethylene vinyl acetate co-polymer) | - | varied from 6:1 to 1:1 depending on circumstances |
| o) | Polyvinyl pyridene                              | - | in water, unspecified concentration               |

The following comments were made by one conservator about the use of Beva 371 in particular. For treatment of objects that were not large-scale, painted on both sides, or in multiple fragments this conservator found that Beva 371 used in very dilute proportions sprayed repeatedly in thin applications to the support fabric only, has provided some very good results and highly recommends its consideration. Its workability enables extremely thin films of this adhesive to be obtained for use in a heat-seal system. However, she also mentions that it is too new as a conservation material for its long-term properties to be known. Artificial ageing investigations indicate reversibility and non-yellowing with time.

#### METHOD OF APPLICATION EG. SPONGING, SPRAYING, FILM ETC.

- 9 conservators spray the adhesive onto their support fabrics.
- 6 painted the adhesive onto the fabric using brushes or paint rollers.
- 9 mentioned casting a film of adhesive onto the support fabric.
- 1 applied the adhesive in a series of dots by squeezing it through a grid onto the fabric.
- 1 used a needlehead (joining of splits through paint and fabric?).
- 4 sponged the adhesive onto the support fabric.
- 2 immersed the support fabric in the adhesive.

#### DO YOU EVER STICK OVER PAINTED AREAS?

14 said that they would consider sticking over painted areas if found to be strictly necessary, while 8 stated that they would never stick over painted areas. One conservator mentioned sticking under (?) painted areas, while another said that adhesion draws paint from the surface.

#### METHOD OF SEALING THE SUPPORT TO THE TEXTILE EG. HOT TABLE, SPATULA, WATER EVAPORATION ETC.

- 15 conservators used heated spatula irons for sealing the support to the textile.
- 6 used a hot table.
- 8 used a small domestic iron.
- 2 used a cold vacuum table.
- 4 rely on solvent evaporation for sealing the support to the textile.

### 10. STITCHING METHODS

#### WHAT TYPE OF THREAD DO YOU USE WITH WHAT FABRICS?

In general people used a stitching thread that was sympathetic to the fabrics they were using and tended not to have particularly rigid uses for each type of thread. The following stitching threads have been used:-

- 7 conservators used silk (in varying thicknesses) for all their stitching, including pulled thread from silk Crepeline.
- 7 conservators preferred to use like fibres with like fabrics.
- Several conservators mentioned the desirability of using a weaker stitching thread than that of the original.
- 9 conservators mentioned the use of cotton thread often in conjunction with cotton fabrics.
- Pulled threads from polyester Stabiltex and other polyester threads (ie. Zwicky, Gutermann's and Skala) were mentioned by 9 conservators; these were used on a variety of fabrics.

#### DO YOU FOLLOW ANY PARTICULAR PATTERN OF STITCHING AND IF SO WHICH ONE?

5 conservators did not follow any particular pattern but tended to use a variety of methods, depending on the object.

One conservator mentioned stitching randomly along grid lines. 22 conservators did use various patterns of stitching, and the following were mentioned:-

- The most widely used pattern consisted of vertical or horizontal alternating rows of running stitches placed at appropriate intervals, (ie. a grid or brick-work pattern) depending on painted areas and the size of the flag.
- Continuous lines of stitching placed at appropriate intervals across the flag.
- Some conservators preferred to stitch around outer edges of a banner and either stitch around the central design or simply around holes, or couch down splits in the central area.
- One conservator mentioned trying to place the stitch on the front at places colours change, not solid colour areas.
- A further question that was raised appears to cause much consternation between conservators in North America, they asked whether "you couch textiles (sewing) with the support cloth tightly stretched on a frame or not?"

HOW DO YOU COPE WITH PAINTED AREAS WHEN STITCHING? (EG. ROUND MOTIFS, THROUGH SLITS ETC.)

No one would stitch through paint, although slits in these areas may be sewn to provide some form of support; while loose fragments are often held in the sandwich of support fabrics by stitching around their perimeters. Long stitches may also be placed across, spanning the surface of a painted area.

11. HAVE YOUR PRESENT METHODS DIFFERED FROM THOSE USED IN THE PAST? WHY DID YOU CHANGE THESE METHODS?

4 conservators felt that they had not changed their methods from those used in the past. Others mentioned various changes particularly a return to stitching rather than sticking techniques, although the dangers of too much stitching were mentioned as doing more harm than good. Some were using less adhesive when they did apply such techniques. Changes to alternative adhesives were also mentioned specifically, eg. starch is sometimes replaced by methylhydroxy ethyl cellulose because the latter can be used with organic solvents, and is less sensitive to mould growth. There also appears to be an increase in testing of a wider range of adhesives, in the hope of finding more suitable ones.

Conservators also mentioned the value of co-operation between other conservation disciplines and conservation scientists. Collaboration with paintings conservators has been found to be particularly useful in several cases. The value of continuously upgrading and improving treatments, while closely monitoring the results and behaviour is a very important need with so many different techniques in use.

12. DOES THE FACT THAT A TEXTILE IS PAINTED AFFECT YOUR CHOICE OF STORAGE OR DISPLAY METHODS? IF YES, IN WHAT WAY IS IT AFFECTED?

With one exception everyone said that painted textiles would affect their choice of storage and display methods, with the majority mentioning the desirability of keeping them flat if possible, at all times. If flags had to be rolled during storage the importance of using as large a diameter roller as possible, was mentioned (eg. one metre diameter was suggested by one conservator) as well as ensuring the flag was rolled with the paint side out. It must then be suspended away from a flat surface to minimise paint deformation. The importance of ensuring that the paint layers are well adhered to the support and are in sound condition (eg. not powdering, embrittled or distorted) before being rolled, stored or displayed was stressed. Care must be taken to isolate from the risk of adhesion when rolling a PVAcetate treated banner. A number of conservators will display flags hanging provided the flag is in suitable condition and has an appropriate support system. Several mentioned using various pressure mount systems sometimes in conjunction with a padding material and Plexiglas. Hanging flags for short periods of time such as three months in every 5 years was also recommended as a means of minimising any damaging effects from display. Stitching to a board and specially constructed, conditioned cases or framing and glazing were suggested as methods of display. The importance of correct climate and lighting control was discussed and notice given to the needs of both the textile and painted areas. Small museums in Canada have particular problems where the RH may vary from



85% in the Summer to 20% in the Winter. This has to be kept in mind when devising any conservation treatment.

### 13. ANY OTHER POINTS

There were various points that were brought up in this section, many related to observations people had made during their work on painted flags and banners. These comments have been included in the relevant sections of the paper.

### Conclusion

When comparing the results from the questionnaire, the variety of conservation treatments applied to flags and banners became apparent. Although quite a high proportion of conservators considered washing their painted textiles and generally tested carefully before proceeding with this particularly hazardous operation, we were still slightly surprised by the number of conservators that had noticed and apparently accepted slight paint loss during washing. This perhaps suggests that more work and discussion is needed in the area of pre-washing consolidation methods and materials.

Particular differences were noted in the way adhesives were used both as consolidants and when used in conjunction with support fabrics. There were many types of adhesives used and the concentrations in which they were applied varied considerably. The general feeling of conservators seemed to be in favour of a return to the use of stitching techniques where possible, rather than adhesive methods, perhaps due mainly to the general concern regarding ageing characteristics of adhesives.

The stitching techniques were also quite varied with many different stitching patterns and threads in use. There also appeared to be differing opinions affecting the choice of stitching threads, with some conservators mentioning the desirability of using a weaker stitching thread than the original, while others preferred to use stronger synthetic threads.

The majority of conservators had similar views concerning the storage and display of painted textiles, the following comment, from a conservator summing up the problems inherent in flags: "The philosophical concerns with flags - historical, emotional, two-sidedness, drape, battle stains and scars and repairs, their simultaneous abundance and particularity make them difficult even before the practical problems are tackled. The issue of reproduction is interesting in this context."

The importance of adapting different techniques for each individual flag was stressed, with several conservators mentioning that they still had a long way to go before finding a satisfactory answer to the problem of conserving painted flags and banners. We hope that these findings and our own work (2) will help to form the basis for further research into this area.

We would like to thank all those conservators who gave up their time to reply to the questionnaire and hope that the results may be of interest to those in this field.

### References

1. Ilona Laki, "The Restoration of a One-piece Banner Painted on Both Sides." Preprints, IV International Restorer Seminar, Vezprem 1983. Institute of Conservation and Methodology of Museums.
2. N.T. Muir and N.S. Yates, "The Treatment of Painted Flags and Banners at the National Maritime Museum, Greenwich". ICOM 8th Triennial Meeting, Sydney, 1987.









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